EVALUATION OF POLYMERIC MATERIALS AS LOSS CIRCULATION AGENTS IN SHALLOW ZONES

BY

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Dedicated to my beloved Parents for their Prayers, Endless Love and Support through my research work

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THESIS ABSTRACT (ENGLISH)

Full Name : Mohammed Omer

Thesis Title : Evaluation of Polymeric Materials as Loss Circulation Agents In Shallow Zone

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Drilling oil wells is burdened with a large number of technical and economical problems that often makes it unprofitable or difficult to further develop some of the fields. One of the most commonly occurring problems during drilling an oil well is Lost Circulation. Lost circulation is the continuous loss of drilling fluid when it encounters fractures, high permeable zones or pore spaces, during drilling. Lost circulation can lead to blowout endangering the life and causing serious damages to the equipment [1]. Polymeric materials such as polyacrylamide can be used as Lost Circulation Materials (LCMs) to seal the fractures and prevent the drilling fluid from entering into them.

The aim of this thesis is to study the rheological properties of the polymeric materials used in preparation of LCM for combating loss of circulation while drilling at shallow zones by studying the rheological properties of different concentration of a polymer and studying the effect of magnesium, manganese, calcium and ferric ions and organic crosslinker polyethyleneimine on the viscosity and thermal stability of polyacrylamide (PAM).

The major findings of this research thesis include the variation in viscosity profile, effect on elastic modulus and reduction in the thermal stability of the PAM on the addition of counterions and crosslinker to enhance viscosity of PAM to form a gelation.

THESIS ABSTRACT (ARABIC)

الاسم : محمد عمر

العنوان: تقييم المواد البوليمرية كعوامل فقدان الدورة في المناطق الضحلة

التخصص: هندسة بترولية

التاريخ: ديسمبر 2012

حفر الابار النفطية يصحبه عدد من المشاكل التقنية والاقتصادية التي غالبا ما يجعل تطوير بعض الحقول غير مربح أو امراً صعباً. واحدة من أكثر المشاكل شيوعا التي تحدث أثناء حفر بئر نفطي هي فقدان دورة سوائل الحفر . فقدان دورة سائل الحفر يستمرعندما يواجه الكسور أو المناطق ذات النفاذية العالية أو الفراغات المسامية أثناء الحفر. فقدان الدورة قد يؤدي الى الانفجار وهذا يهدد الحياة ويسبب أضرارا رهيبة للمعدات. ويمكن استخدام المواد البوليمرية مثل بولكرلميد كمواد فقدان الدورة (LCMs) لسد الكسور ومنع دخول سائل الحفر إليها.

الهدف من هذه الرسالة هو دراسة الخصائص الريولوجية للمواد البوليمرية المستخدمة في إعداد المواد المانعة لفقدان سوائل الحفر LCM اثناء الحفر في المناطق الضحلة من خلال دراسة الخصائص الريولوجية لتراكيز مختلفة من البوليمر, ودراسة تأثيرأيونات كل من المغنيسيوم والمنغنيز والكالسيوم والحديد, و عابر الروابط العضوية البوليثيلينمين على اللزوجة و الاستقرارالحراري للبولكرلميد (PAM).

النتائج الرئيسية لهذه الأطروحة البحثية تشمل التباين في مظهراللزوجة والتأثير على معامل المرونة والانخفاض في الاستقرار الحراري لل PAM من خلال إضافة مكافح الأيونات و عابر الروابط لتعزيز لزوجة ال PAM من أجل تشكيل الهلام.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول و المعادن

الظهران المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

During drilling of oil and gas wells, drilling fluids are circulated through the drillstring assembly and drill bit into the wellbore for removing the drill cuttings. This drilling fluid also maintains a predetermined hydrostatic pressure to balance the formation pressure. Drilling fluid is recirculated again and again into the well, since it is expensive. When low pressure subterranean zones are encountered while drilling, there is an appreciable loss of this drilling fluid. Lost circulation is defined as the loss of appreciable part or entire volume of drilling fluid through the borehole into the cavernous, vuggy, fractured and highly porous formations [2]. During drilling, lost circulation problem is common and frequent. This has presented one of the greatest problems to the petroleum industry.

1.1 Types of formations/zones causing loss circulation

The following types of formations or zones cause the lost circulation problem in general.

- Cavernous or Vugular formations
- Unconsolidated zones
- High permeable zones
- Naturally or artificial fractured formations

If the severity of loss of drilling fluids is between 1 bbl/hour and 10 bbl/hour then it is known as seepage loss**.** If the losses exceeds 10 bbl/hour but is less than 50 bbl/hour it is

defined as a partial loss. The loss is said to be complete loss when there is around 500 bbl/hour losses [3].

Figure 1, below shows a cross-section of a well, with fractures in the formation. The drilling fluid is represented by blue color is going into these fractures or high permeable zones or highly permeable formations and thereby causing loss circulation of drilling fluid.

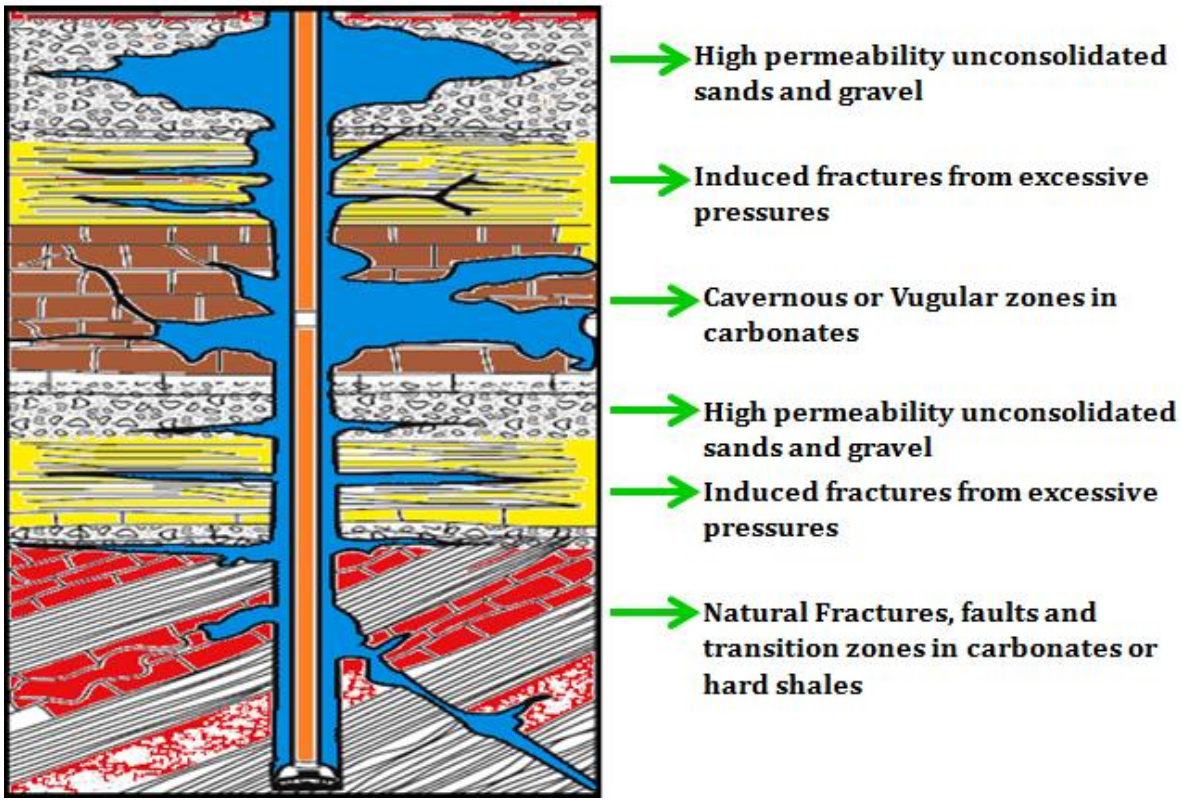

Figure 1: Types of formations causing losses

The 'lost circulation' problem can be reduced by introducing lost circulation materials (LCMs) into the well bore to seal the zones. Various materials can be used to seal these lost circulation zones formed by porous, permeable zones and fracture zones by materials such as gels, polymers [4]. Lost circulation materials are classified according to their

properties and applications such as formation bridging LCMs and seepage loss LCMs. They are classified into three categories: bridging agents, gelling agents and cementing agents. Bridging agents are the ones which plug the pore throat, vugs and fractures in loss circulation formations. Bridging agents are ground peanut shells, walnut shells, cottonseed hulls, mica, cellophane, calcium carbonate, plant fibers, swell-able clays ground rubber and polymeric materials [5]. Gelling agents and cementing agents are used for transportation and placement of the bridging agent at the appropriate place in the loss circulation zone. Water absorbent cross-linked polymers are used in this case. The LCMs are evaluated on their sealing properties both at low differential pressure and low temperature and at HTHP conditions. The effectiveness of the LCM gel in sealing the zones is checked for various pressures.

These drilling problems are encountered both in on-shore and offshore fields whenever the formations are weak, fractured or unconsolidated. Drilling for oil and gas in deep water encounters further challenges brought about by various reasons like gas kicks, blowouts, presence of unconsolidated sand formations, shallow gas, gas hydrate, lost circulation, sea floor washout, borehole erosion [4]. These problems are hazardous and also cause significant increase in the drilling cost. For the analysis of various losses a case study was taken from Marathon Oil Company. Figure 2 represents various problems encountered while drilling 5 offshore wells of *Marathon Oil Company*. Various losses like weather, cementing, stuck pipe, well control, hole instability, lost circulation and mechanical might occur while drilling a well. These losses consume the time and hence increases the drilling time thereby increasing the drilling cost. Marathon Oil Company's

drilling was interrupted for 9 days due to Lost Circulation problem and this leads to huge increase in drilling cost, labor cost, loss of drilling fluid, reduction in the hydrostatic pressure. Hence lost circulation of drilling fluid is one of the major problems that should be solved. The motive of this research is to mainly focus on studying the behaviour of LCM, which is used to solve the Lost Circulation problem.

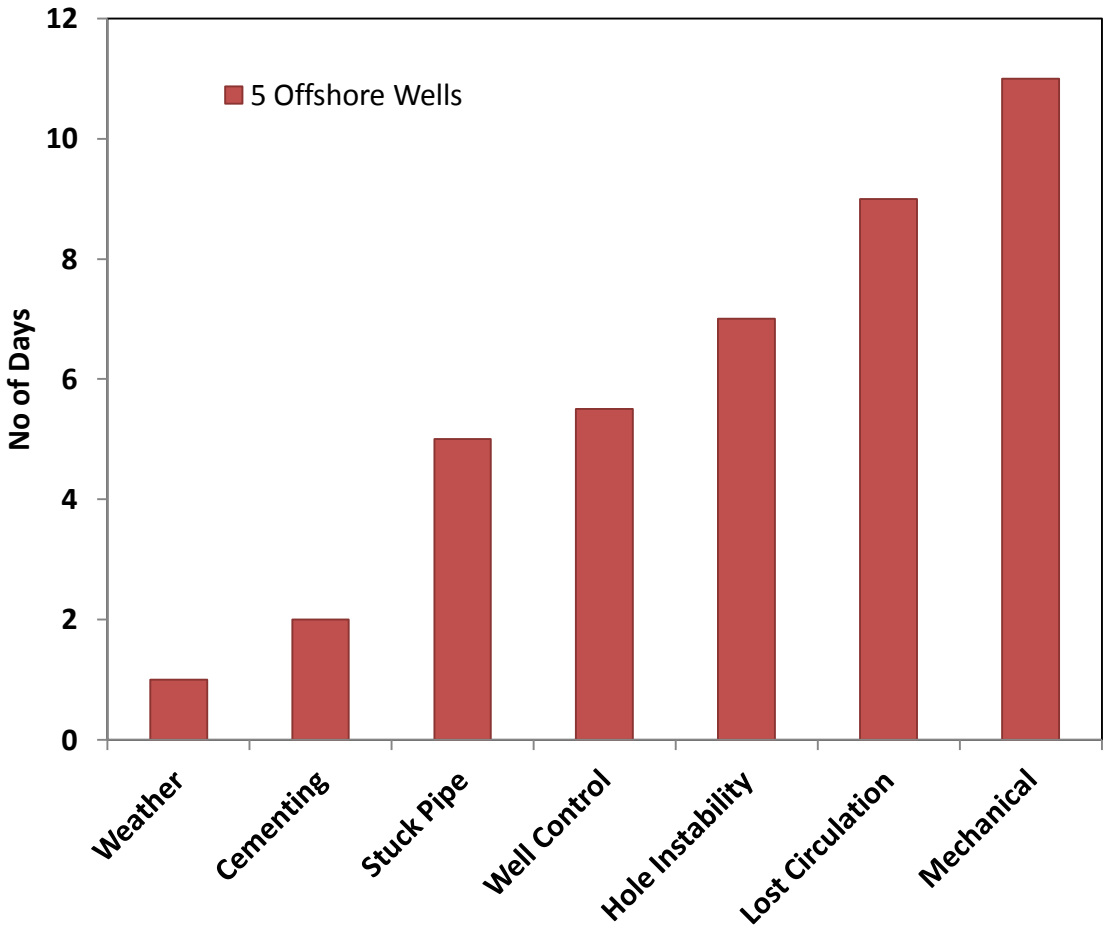

Figure 2: Problems in Drilling Oil wells [6]

1.2 Objective

1. To review the existing practices for controlling loss circulation of drilling fluids using polymers.

2. Studying the rheological properties of different classes of polyaclyramide (PAM) at various concentrations

3. Investigate the effect of counterions(Ca^{2+}, Mn^{2+}, Mg^{2+}, Fe^{3+}) on the viscosity profile of PAM

4. Evaluate the mechanisms by which polymer materials work as LCM.

5. Develop a see-through cell to evaluate the flow, sealing, blocking & stability of LCMs at room temperature

CHAPTER 2

LITERATURE REVIEW

2.1 Drilling fluid

It is a fluid which is circulated during drilling from the surface through the interior of the drill string and the annulus of the drill string and formation. The drilling fluid is also known as drilling mud [7].

2.1.1 Importance of Drilling Fluid to Petroleum Industry:

The drilling fluid suspends and transport solid particles to the surface for screening out and disposal. It is used for preventing unwanted fluids from mixing with and degrading the rheological profile of drilling mud and to prevent the loss of downhole pressure from fluid loss should the borehole traverse an interval of porous formation material. Drilling fluid keeps suspended weighing agent, drilling cuttings and other solids so that the entire column of drilling fluid is not interrupted else would tend to reduce downhole pressure, as well as creating a “blowout” in which the fluid and even the drill string are violently ejected from the well, with resulting catastrophic damages, particularly from fires. It is also a very good lubricant to the drill bit. Hence due to the various above reasons, drilling fluid needs to be re-circulated and we need various mechanisms or plugs to seal the fractures or vugs or pore spaces or highly permeable regions. Various plugs or Lost Circulation Materials have been designed to reduce lost circulation

2.2 Polymers as a Lost Circulation Material

Polymers have been used in drilling fluids for lost circulation materials since a long time [4, 5 and 7]. Since that time, polymers have become more specialized and their acceptance has increased accordingly. Polymers are part of practically every water-based system in use today. Indeed, some systems are totally polymer dependent and are termed broadly as polymer systems.

A polymer is a large molecule comprised of small, identical, repeating units. The small, recurring units are called *monomers.* Polymerization occurs when the monomers are joined together to form the large polymer molecule. Polymers may have molecular weights in the millions or they may consist of only a few repeating units. The polymers used in drilling fluids come in three types:

- Naturally occurring
- Modified naturally occurring
- Synthetically derived

2.3 Composition of Lost Circulation Material

A lost circulation material is mixed with drilling fluid and sent downhole. Once it encounters a fracture, owing to triggering mechanisms it is activated. The LCM consisting of Polymers expands in presence of water is due to electrostatic repulsion between charge sites on the co-polymers [8] and seals the fracture. Lost circulation material can be flakes, fibers**,** sized marble, nut plug, cotton seeds, sized mica, water-soluble polymers, crosslinking agents and fibers [5]. The fibers have been extensively used to increase toughness. Fibers like Nylon and polypropylene are mixed with the

cement slurries either as plugs in open holes or during primary cementing operations were also introduced [4]. In some cases the spacers [5] are added immediately after the drilling fluid, prior to the injection of lost circulation material. This is done to clean surface and also the spacers, acts as buffers between mud and pill to prevent contamination, and ensure water wet surface. Amanullah & Boyle (2006) designed a multifunctional, environmental friendly and economic gel which was able to show nearly 100% blocking efficiency and this gel was unaffected by salinity of water

The gel formed due to swelling of polymer will again be reverted back into fluid state due to addition of highly concentrated salt solution due to the screening of the charged site on the copolymer [8].

2.4 Existing Lost Circulation Practices

Due to development of technology various types of LCMs are being designed to suit different requirements downhole to combat the lost circulation problems. The main objective of each lost circulation additive is to control or reduce loss of drilling fluid downhole.

An additive for drilling fluid was designed to block pre-existing and induced fractures. The additive comprises of Graphitic and Polypropylene granules with diameter between 1000-200 microns [7], was used with Oil Based Mud.

LCM capable of reducing the losses while drilling comprises of a base fluid, a mixture of particles and a blend of fibers. Also the spacer is used as a buffer between LCM and drilling Fluid to clean up the impurities and ensure the water wet surface. It is used with a water based pill. The blend of solid particles which are oil swellable and rigid flexible

fibers are then added to aqueous base fluid. Spacers like siloxanes, silicones, barium sulphates, calcium carbonates, sodium silicates, poly-paraphenyleneterephthalamide and oil swellable materials were neoprene rubber, natural rubber, nitrite rubber, acrylate butadiene rubber, polyacrylate rubber, brominated butyl rubber, flouro rubber, silicone rubber. Fibers comprises of glass fiber, polypropelene fiber, polyaramide fiber, polyethylene fiber and organic fibers. This LCM designed was functional with both water-based and oil-based muds [5]. Figure 3 shows the various practices used to seal the largest fractures effectively. According to *Howard & Scott (1998),* a granular material was effective in sealing largest fractures or openings.

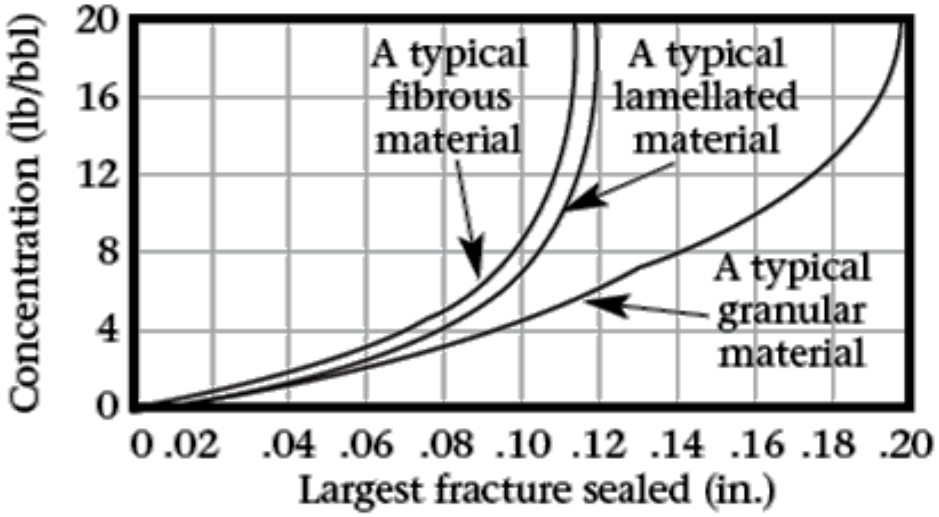

Figure 3: Effect of types of Material on Sealing Fractures (Courtesy: *Howard & Scott 1998)*

Fibers when mixed with polymeric materials add strength to the lost circulation material and help in sealing the fractures by forming a mesh. Fibers are mixed with the gelation solution and pumped to the subterranean region formation [9]. The composition of gelation solution consisted of a partially hydrolyzed polymer of carboxylate containing

polymer made from hydrolyzed polyaclyramide, Crosslinker chromic III carboxylate complex, this crosslinker was made by adding electropositive chromium III and electronegative carboxylate obtained from formic acid, lactic acid, propionoc acid and finally the last material in the mixture are fibers like glass, cellulose, carbon, silicon, graphite, calcined petroleum coke.

Cements are also used for treating the lost circulation problems. The cement system composition included cement slurry, water and a super absorbent polymer [8] which in presence of water forms a gel or a solid like structure. The super-absorbent polymers like *2-propenamide-co-2-propenoic acid, sodium salt and sodium polyacrylate* [8] were used. These polymers swelled in presence of water due to electrostatic repulsion between charge sites on the co-polymers. Once the drilling was completed the gels were again reverted to liquid state on addition of *33% of NaCl* solution was added to *15.8 ppg cement slurry* [8] to convert the gel back into slurry.

For clay formations a special type of material known as Expanded Aggregate [10] was used a LCM. Expanded Aggregate was made from clay bearing soils. These soils are mined with connate water present, crushed, and put through rotary kilns, the soil is fired from 1000-1800°F which results in its vitrification.

Polymers are mixed with cross linkers to add strength and are presently most widely used in preparation LCM. In a successful existing LCM, cross-linking polymer pills were pumped to seal the loss zones and restore circulation. The fluid system consisting of a mixture of Calcium Aluminum Silicate (CAS) [11] reacts to form a complex with pre-dispersed Bentonite to form a shear thinning fluid with unusual rheological properties. El

hassan et al., (2003) developed a new system incorporating silica based fibers called advanced-fiber cement system (AFCS). These AFCS fibers are highly flexible and are mixed with cement slurries. AFCS is a newly developed system that incorporated silica based fibers for cement slurry applications. These fibers had a cylindrical shape with an average length of 0.5 in. and a diameter of about 20 microns [12]. AFCS formed a fibrous network across highly permeable formations, induced and natural fractures, and Vugular formations to prevent and stop the losses during remedial or primary cementing operations. AFCS doesn't plug surface and downhole equipment and are easy to disperse.

In 2005, Fang et al.,(2005) designed a super absorbent polymer (SAP), expands volume after encountering the fluids downhole and forms plugging in fractures [13]. Crosslinked polyacrylamide and polyacrylate [13] are used in combination with other LCM materials to reduce fluid loss. Nano-composite gels [14] are also used in lost circulation treatment. Also Zirconium [15] is being used in many cases to cross-link with Polyacrylamide.

Water-based drilling fluid known as *Universal Fluid (UF)* [16] was treated with finely ground blast furnace slag and gets concentrated in the filter cake formed while drilling permeable formations and slowly sets to form a hard layer intimately bonded to the formation and is used as an LCM. Another invasion control drilling fluid was developed to drill reservoirs prone to lost circulation. This fluid combines certain surfactants and polymers to create a system of micro-bubbles known as *Aphrons* [17] that are encapsulated in a viscosified system. These *Aphrons* are non-coalescing, and create a micro-bubble network to stop and slow the entry of fluids into the formation. The viscosity builds to create a resistance to movement into and through the zone [17].

To design a lost circulation material, rheological studies need to be conducted to study the behaviour of the lost circulation agents. Various studies have been carried out to study the effect of various cross linkers like Chromium (III) Acetate Gelation [18], polyethyleneimine [19] on Polyacrylamide. Effect of Cr(III) on polyacrylamide, increases the gelation time defined with respect to viscosity raise, increases with shear rate for the high-molecular-weight non-Newtonian formulation [18], and remains unaffected by shear for the low-molecular weight Newtonian formulation and gel strength is independent of shear rate history [18]. From the literature it was deduced that Polyacrylamide (PAM) is being used as one of the main constituent in the LCM and more over it is easily available and can withstand high temperatures. Since the formation has high temperatures PAM is capable of withstanding these temperatures without degradation.

Scott, et al. (1955) conducted laboratory and field tests for improving techniques for the controlling of loss of circulation of drilling fluids and to determine effects of lost circulation materials on drilling fluids and drilling rates [20]. The physical properties of granular materials most suited for use in drilling fluids to seal fractures were found to be angularity, low specific gravity, high compressive strength, low modulus of elasticity and low hardness factor [20]. They proved that materials possessing low specific gravity, high compressive strength, low modulus of elasticity and low hardness factor and graded in particle size from 30 mesh to 100 mesh, so as to pass through a shale shaker screen, reduce circulation losses to induced fractures. Also, these materials improved the lubricity of drilling fluids [20].

Also cutting action of rotary rock bits is not impaired by the addition of lost circulation materials to the drilling fluids and mixtures of coarse, granular materials and solid, oil-

soluble materials prevented loss of drilling fluid in oil bearing formations and did not impede subsequent flow of oil from these formations. It was concluded that a slurry of diesel oil- Bentonite-cement will plug severe lost circulation zones containing natural fractures and vugs [20].

Polyglycolic Acid (PGA) and Polylactic Acid (PLA) are also being used as LCM are capable of sealing fractures for drilling low temperature wells up to 60ºC [21] and also the fibrous PGA and PLA transport cuttings from well bottom as PGA has the high strength during the first several hours. This paper emphasized that as the mud weight is increased, mixing lost circulation materials with enhancing cutting transport capability is important to conserve the mud volume.

High resiliency graphitic carbon, which contains 99.9% carbon, is also being used as LCM [22]. This research developed laboratory methods to characterize the resiliency of different graphitic carbons and also demonstrated that other LCMs are less resilient when compared to graphitic carbon. RGC characteristics related to resiliency, lubricity, resistance to attrition were validated and compatibility with downhole tools, making it a versatile material for most LCM combinations [22].

The effect of mechanical properties of LCMs on wellbore strengthening were investigated using compression/crush tests at different confining pressures simulating a wide range of to fracture closure stresses (FCS) [23]. As per the results crush test demonstrated compaction and significant crushing of the ground marble and ground nut shells at high confining pressure approximately around 5000 Psi [23]. Crushing resistance and resiliency of these materials was improved by small additions of resilient graphitic

carbon (RGC). Finally this paper recommends different combinations of LCM that can be used to provide wellbore strengthening effectively.

A low LCM pill was specially designed for pay zones to seal temporarily or indefinitely critical intervals loss circulation zones in places where drilling and cementing operations are very difficult. This formulation was prepared using invert emulsion, cross-linked with magnesia [24], up to 90% soluble. The phase change of invert emulsion and addition of light burned magnesia form the viscous fluid and remains stable till activator is not added. By addition of activator, control process of static gelation starts and forms the magnesia cement. Such formulations have sp gr 1.10-1.45 and stable at high temperature upto 120^{o}C with a viscosity of 45-60 cp. This pill can be retarded for desired time of placement and is also soluble in 15% HCl [24].

This paper focuses on use of technology to predict lost circulation to plan ahead of the schedule Proprietary hydraulic design software (HDS) [25] should be used to predict the equivalent circulating density (ECD) over an interval in one module, calculating the fracture width and thereby selecting and designing a proper material and particle size distribution that can efficiently plug that fracture in a second module. The third module is used to predict the change in rheology [25] after adding the lost circulation materials and going full cycle to update circulating density data.

Also for saving costs and time the design strategy, formulations and testing requirements, placement techniques and procedures are required to successfully squeeze large-volume of cement to remediate severe, high-rate, large-volume losses [26]. This was successfully implemented in two deepwater case studies. Cement squeezes can be performed through

many bottomhole drilling assemblies, where conditions require, and eliminate the dependence of success on correct sizing of bridging particles. Large-volume, specially designed cement squeezes have proven effective methods to restore wellbore integrity after loss rates as high as 320 to 480 bbl/hr and total volume of losses to the formation of up to 4000 bbl prior to treatment [26].

A new high-fluid-loss, high-strength (HFHS) [27] pill system was developed and optimized meets field criteria for addressing lost circulation problems. As per this research HFHS pill system works over a wide range of loss rates providing effective and stronger seal when compared to traditional treatments.

A more efficient tool using innovative shifting technology [28] for the placing lost circulation materials (LCM) that does not require the exorbitant lost time and complicated cycling methods of the current technology has been designed. This tool provides unlimited open or close cycles in a simple manner. As per this technology, drillers can shift an unlimited number of times and in as little as 5% of the time required by conventional tools [28]. These capabilities result in direct reduction of lost time operating the tool as well as a quantifiable reduction in fluids lost while operating the tool. It was concluded that the use of this innovative circulating technology has assisted a major service company in reducing downtime and excessive costs during lost circulation events [28].

A fibrous lost circulation pill has been developed which does not require any activators, retarders, set time calculations, or temperature activation and is specifically designed for rapid mixing and pumping with minimal equipment [29]. It was concluded from this

research that it is the ability of this fibrous pill slurries to rapidly dewater/de-oil and form a sealing plug on both ceramic filter discs and slotted metal discs. Also this LCM forms a sealing plug in depleted sand formations. This pill can easily be weighted using barite to help control hydrostatic pressures and works well with a wide range of fluids including freshwater, brines, all mud systems and base oils. This product meets strict environmental requirements for use in both the Gulf of Mexico and Norway. It can be rapidly mixed and pumped on location using standard rig equipment and only requires base fluid, barite and the product. The pill formulation is compatible with all mud systems and is easily removed using standard solids control equipment [29].

PEI was crosslinked with HPAM gels for water shut-off applications in china [30]. Also the research paper discussed that gel will form between PEI and PAM even at room temperature and the mircostructure of PEI/HPAM has lot of cavities. It was concluded that gelation time for PEI/PAM is 18-72hrs at 65oC which is longer than Chromium (III) Acetate/HPAM [30]. This gel can also be used as LCM.

2.5 Polyacrylamide/ Polyacrylate copolymer:

Partially hydrolyzed Polyacrylamide (PHPA) is often used to identify the copolymer acrylamides/ acrylate [31]. The end product of a PHPA is formed by acrylamides/ acrylate copolymerization.

During copolymerization, the two monomers are linked together in a randomly and form a linear, carbon-carbon backbone. The resulting copolymer has carboxyl groups and amide groups randomly distributed along its backbone. The resulting copolymer is shown

in Figure 4. Due to the presence of Carbon-Carbon linkage in the polyacrylamide, it has exceptional thermal stability and is resistant to bacteria. [31].

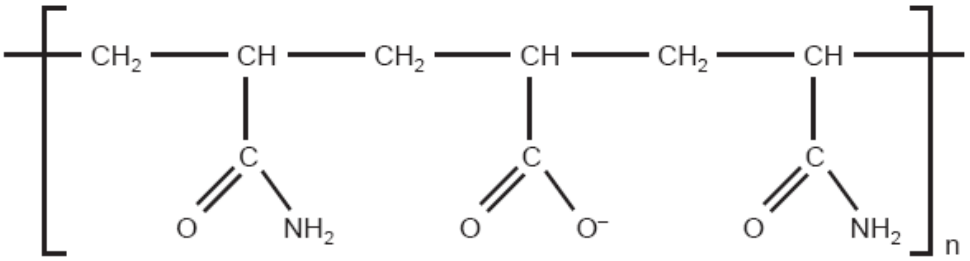

Figure 4: Partially Hydrolyzed Poly-Acrylamide

POLY-PLUS [31] is the most commonly used PHPA in drilling fluids is the high molecular- weight version which is prepared with 65 to 70% acrylamides and the remaining percentage acrylate. Molecular weights range up to 20 million. *POLY-PLUST* is used as a shale inhibitor and solids-encapsulating polymer in freshwater, seawater, NaCl and KCl systems. In addition to its shale-inhibiting properties, it also provides drilled cuttings encapsulation and viscosity in freshwater systems. The shale inhibition feature of PHPA occurs when the polymer attaches to clays on the wellbore and blocks the hydration and dispersion that normally occurs. The anionic carboxyl groups attach to the positive charges on the edges of the clay particles. Since the polymer has a high molecular weight and is relatively long, it combines with several sites along the wellbore [31]. This has the effect of coating the wellbore and restricting water from entering the clay. The same effect is seen on the drilled cuttings. The polymer helps preserve the integrity of the cuttings, which allows for much easier cuttings removal at the surface.

PHPA also aids in shale stabilization by thickening the water phase. PHPA increases the viscosity of the drilling fluid filtrate, which has the effect of limiting the filtrate depth of invasion. Although water may penetrate far into shale, a thick polymer filtrate faces much greater resistance due to the rapid buildup of capillary pressures. This has the effect of reducing the amount of filtrate water available for hydration. It also limits the ability of a filtrate to enter a small fissure or fracture plane within shale.

2.6 Aphrons

Aphrons are bubbles, approximately 10 to 100 microns in diameter and are composed of a gaseous or liquid core with a thin aqueous protective shell [32]. Its stability depends on *Marangoni* [32] effect. The mass transfer along interface between two fluids due to surface tension gradient is known as *Marangoni* effect [33]. If the mass transfer rate is high, aphrons will be unstable. Hence, the shell fluid is designed to have certain viscosity to minimize the *Marangoni* effect. The shell is composed of an inner layer and an outer layer.

Figure 5 illustrates a typical aphron structure, the inner layer consists of surfactant molecules which supports and separates the air core from the viscous layer. The outer layer, which also supports the viscous layer, is hydrophobic outwards and hydrophilic inwards. Since this bubble is in contact with the bulk water, it is believed that there is another layer in which the surfactant molecules are hydrophobic inwards and hydrophilic outwards. This indicates that there is a region in between the aphron outer shell and the bulk phase layer where a hydrophobic globule will be comfortable and, therefore, oil can adhere to the gas aphron.

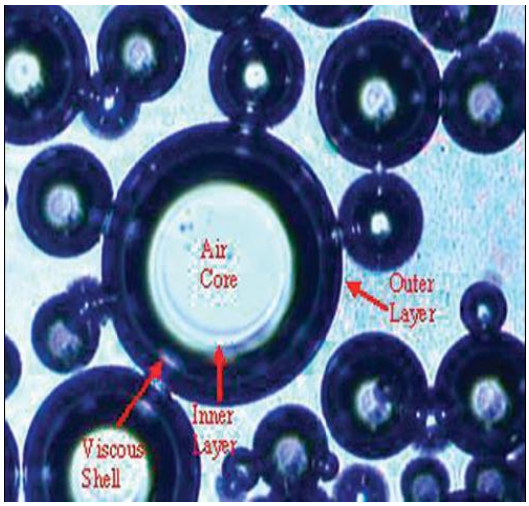

Figure 5: Typical aphron microscope picture [32]

Aphrons consists of the base fluid and the aphronized fluid. An aqueous solution of Xantham Gum [32] solution is used in preparation. For the preparation of Aphronized fluid surfactants like hexadecyltrimethyl ammonium bromide [32], a cationic surfactant and sodium dodecyl benzene sulfonate an anionic surfactant.

Use of Aphrons to reduce the drilling fluid losses

The properties of Aphrons are being utilized to the preparation of lost circulation material. The Aphrons are mixed with drilling fluid and injected downhole for controlling loses. The hydrophobic nature of the Aphrons shell enables Aphrons to clump together yet resist coalescence [34]. When Aphrons are forces into the formation they form large aggregates and create a structure of the deformed cells in the pore throat or fracture tip akin to that of the true formation as shown in Figure 6.

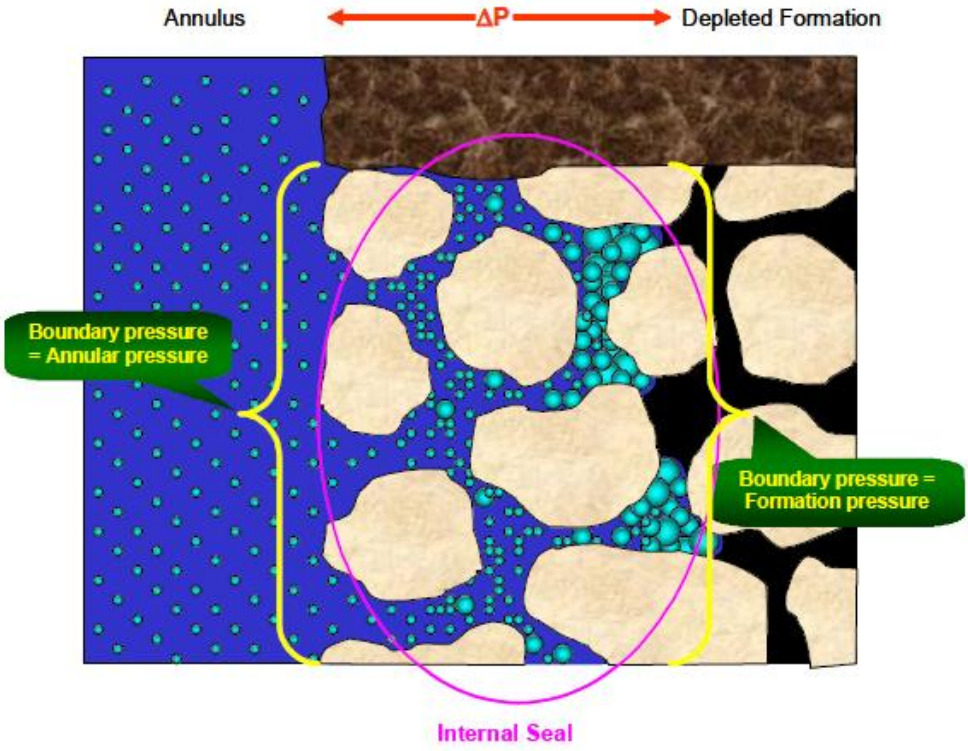

Figure 6: Invasion of Aphron based Drilling fluid into the formation [34]

In case of water wet reservoirs capillary pressure resists intrusion of hydrophobic materials into capillary restrictions in the formations. Before a bubble can be displaced, the pressure differentiated across the bubble must be sufficient to overcome capillary pressure. The effectiveness of the seal depends upon the size of the pore throat and the degree of hydrophobity of the aphron shell. Small openings and strongly hydrophobic bubbles promote sealing [34].

2.7 Functioning of LCM upon entering a Fracture

A cross-section of oil well [7] is shown in Figure 7A with a drill string and drilling fluid flowing represented by yellow color circulating inside the well. The drilling fluid is mixed with blue particles of lost circulation material.

An assumption is made about the pressure inside the well; the pressure exceeds the strength of the formation and thereby causes the fractures to open. The drilling fluid flows into the fracture causing lost circulation of drilling fluid. The lost circulation material mixed with drilling fluid accumulates inside the fracture until the fracture is bridged or plugged by effective amount of the lost circulation material. Once a plug or a seal is formed, there is a pressure drop across it and the tip of the fracture is no longer subjected to full well pressure [7], thereby stopping the growth of the fracture. Figure 7B, illustrates a stage after the LCM has accumulated inside the fracture, the well pressure is reduced and the fracture is closed due to formation of seal. The dashed line in Figure 7B indicates the dimension of the original fracture. In the process of closure, the lost circulation agents in the fracture are compressed by the formation and depending on its properties either reversibly or irreversibly compacted and deformed [7].

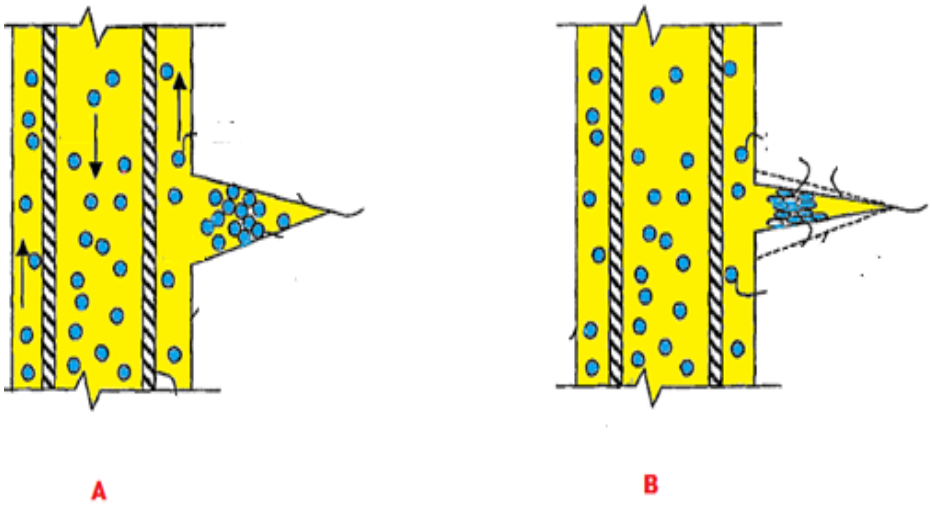

Figure 7: working of LCM [7]

2.8 LCM Practices in Middle East

In Middle East the treatment of downhole fluid losses depends upon the severity of the fluid loss with either conventional or non-conventional LCM available. For seepage and partial losses in non-reservoir sections, conventional LCM with flakes, fibers**,** sized marble, nut plug, cotton seeds, sized mica, frac seal, barofiber [35] are used effectively with an hourly addition of 20-30 ppb [35]. For severe losses coarses conventional LCM is used to reduce the severity with an hourly addition of 30-40 ppb. For total fracture losses Non-conventional LCM like thermally activated polymer, high filtration squeeze and especial long fibers are pumped as slurries through the drill pipe, which forms hard plugs, plugging the Fractures by design particle distribution [35]. Saudi Aramco has classified treatment of LCM according to three different regions/ formations as follows:

2.8.1 Dolomite and Limestone formations: It consists of top holes of width varying from 34″, 28″ and 22″ with total severity. These types of formations are treated with nut plug, fibers, cotton seeds, sized mica. When total losses are experienced, drill water and mud cap is used. In cases where reactive clays are below the loss zone, cement plugs in conjunction with shale inhibited fluid are used. Concentration of LCM pills is 40 ppb when Measurement While Drilling (MWD) tools are used and 80-100 ppb without MWD.

2.8.2 Calcarenite, Limestone and anhydrite formations: It consists of intermediate holes of width varying from 17″, 12 ¼″ with losses varying from partial to total severity. The Preventive treatment is Nut plug, fibers, cotton seeds, sized mica for an active system with 30-40ppb. For reactive clays Cement plugs,

soft plugs, high filtration squeeze pills are used. In cases when well is drilled with high overbalance which lead to total or severe losses, Non-conventional LCM techniques like polymer have been used.

2.8.3 Arab D, Khuff and Unayzah formations: It consists of bottom holes of width varying from 8 ½ ″ to 6 1/8″ and with the losses varying from partial to total severity. The Preventive treatment is done with acid soluble LCM to protect reservoir with concentrations of upto 40ppb is being used with success in highly fractured Khuff reservoir with open hole completion. LCM pills are pumped with maximum 40 ppb through MWD tools. When MWD& Motor are not in the bottom hole assembly (BHA), this concentration used up to 100-120 ppb.

CHAPTER 3

METHODOLOGY

The main objective of this thesis is to study the rheological properties of polymeric materials as lost circulation agents. Somwangthanaroj, T. (2010), defined rheology as the science of deformation and flow of matter under controlled testing conditions. Flow is a type of deformation and deformation is caused due to flow. For all the materials which will be pumped, extended, molded, mixed, chewed, sprayed, transported, heated or cooled, stored [36] Rheology must be carried out to study its behaviour and estimate the consequences for future use.

In this thesis, the rheological properties of Polyaclyramide (PAM) are studied at various concentration and then the effect of counterions (Ca^{2+}, Mn^{2+}, $Mg^{2+}$and Fe^{3+}) on the viscosity profile of PAM are investigated. In addition, the effect of organic crosslinker to form gel with PAM is also studied. PAM is one of the main constituents of the LCM hence rheology of PAM is being carried out to study the effect of shear rate, temperature, counterions on the viscosity profile of the PAM. This study will help in the further synthesis of the lost circulation material.

The study of Rheological properties is carried out using a Hybrid Rheometer DH3 as shown in Figure 8, manufactured by *TA instruments*; Rheometer is used to measure viscosity over a wide range of shear rates and viscoelasticity of fluids, semi-solids and solids [36].

3.1 Rheometer

All the rheology tests were conducted using Hybrid Rheometer with a Peltier Concentric 40 mm diameter cylinder arrangement from *TA Instruments*. The peltier concentric cylinder system consists of a jacket, an inner cylinder, and a rotor. This arrangement is used for fluid having viscosity from low to medium Range. Figure 8 is the schematic representation the concentric cylinder. This instrument also has robust construction enabling us to run long duration tests. The operation of the system and plotting of the experimental results is done using *TRIOS* [37] software.

Figure 8: Rheometer with concentric cylinder arrangement [38]

3.2 Theory of Rheology

Viscosity is the most important parameter measured in rheology experiments**.** It is defined as resistance to sweep and it is measure as the ratio of shear stress and shear rate. The instrument records the viscosity data in terms of Pascal second units. Properties like storage modulus and loss modulus define gel strength and represent structural information of the compound. Hence these parameters are important to design gel formulations depending upon requirements. Storage modulus (G′) is the ability of PAM to store energy and elasticity of material can be studied and whereas loss modulus (G″) is the ability of PAM to dissipate energy as heat.

Another important parameter is dynamic viscosity (η')**,** it the resistance to flow encountered when one layer or plane of fluid attempts to move over another identical layer or plane of fluid at a given speed and is also called absolute viscosity**.** Out of phase component of viscosity (η″) is the ratio of the storage modulus to the angular frequency, determined during forced harmonic oscillation.

3.3 Types of Rheological tests

1. ***Oscillating amplitude test:*** This test is conducted to determine the Linear Viscoelastic Region (LVR). LVR is the region in a material where stress & strain are related linearly; i.e. where modulus is independent of stress or strain used. All subsequent tests require an amplitude or strain percentage found in the LVR. It was conducted at room temperature of 25^{o}C and atmospheric pressure for a torque range between 1 and 1000 µNm.

2. ***Oscillating frequency test:*** The main objective of this test is to study the effect of angular velocity on modulus and dynamic viscosity at constant strain within the linear viscoelastic region. It was conducted at room temperature of 25^{o}C, atmospheric pressure at a 10% strain and a frequency range between 0.01 and 100 Hz

3. ***Flow sweep test:*** This test is conducted to study the effect of shear rate on the viscosity of the material. The results of this test will also help us determine whether a material is shear thinning or shear thickening. By fitting models like Carreau, the zero shear rate viscosity is obtained from this test. It was conducted at room temperature of 25^{o}C, atmospheric pressure at a 10 % strain and a torque range between 1 and 100 µN-m

4. ***Oscillation temperature ramp:*** The thermal stability of the Polymer was tested by conducting oscillating temperature ramp. The material is subjected to increase in temperature at regular intervals from 25^{o}C – 70^{o}C, at a 10% strain and a frequency of 1.5911 Hz and the stability of the material is obtained.

3.4 Carreau viscosity model:

The effect of shear rate on the viscosity can be described by a nonlinear regression of Carreau viscosity [39] model as follows

$$(\eta - \eta_\infty) / (\eta_o - \eta_\infty) = [1 + (\lambda\gamma)^2]^{(n-1)/2}$$

Where η is the viscosity, η_o is zero shear rate viscosity, η_∞ is infinite shear rate viscosity, λ is time constant, γ is shear rate and n is fluid behaviour index. For all the plots of shear

rate v/s viscosity, Carreau viscosity model was best fit using non-linear regression to obtain the zero shear rate viscosity for further analysis.

3.5 Sample preparation

3.5.1 Polyacrylamide Solution

The Polyacrylamide is in the form of a white powder obtained from *SNF Floerger* with trade name Flopaam 3330S. It is an anionic PAM with 25-30% degree of hydrolysis was discussed by Flaatent et al., 2009 & Kim et al, 2010 and 8 million Dalton as molecular weight. From the detailed literature review [5, 7, 15, 18, 19 and 27] conducted to review the recent practices of polymeric materials used in the preparation of LCM and due carbon-carbon linkage arrangement, it has been concluded that PAM is highly suitable as a LCM due to its high thermal stability and bacterial resistant [31] property. Anionic PAM is used in water shut-off applications as it has moderate negative charges. These negative charges repel and form a network of chains which causes resistance to flow.

Figure 9 shows the chemical structure of partially hydrolyzed PAM which was used in thesis experimentation. The left molecule is the amino group and the right is a carboxyl functional group. The amount of Hydrolysis level is defined by the mole percentage of the carboxyl functional groups among the total functional groups.

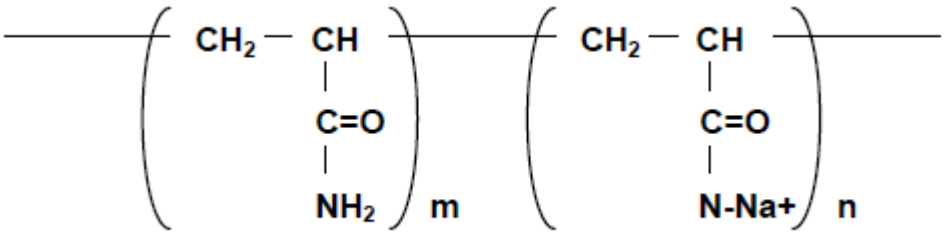

Figure 9: Flopaam Chemical Structure
(Flaatent et al., 2009)

The Table 1 shows the various concentrations of Polyacrylamide prepared for conducting the tests. The minimum concentration is considered as 0.05% by wt and is increased upto 1% to study the effect of PAM concentration. The solution is prepared by dissolving wt% of PAM in distilled water. The procedure as per *SNF Floerger* [40] is to weigh the required quantity of PAM and gently pouring inside the beaker containing the specified amount of distilled water. The mixture of PAM and distilled water is stirred using a magnetic stirrer until the flakes of PAM are completely dissolved and forms a clear solution with distilled water. The stirring will take around 7-10 hours depending on the concentration of the PAM. Higher the concentration of the PAM, more is the stirring time.

Table 1: Sample preparation of PAM

PAM	PAM	Distilled Water	Status
wt %	gm	ml	PAM + Water
1	2.5	250	Dissolved
0.5	1.25	250	Dissolved
0.1	0.25	250	Dissolved
0.05	0.125	250	Dissolved

3.5.2 Polyacrylamide/ Counterion

There is innumerable research work done in the field of lost circulation of drilling fluids covering areas like sealing effectiveness of the LCM, types of materials used in the LCM, rheological properties of the LCM. LCM is used with the drilling fluid which contains ions calcium [41], sometimes sea water is used in drilling fluid which might have the presence of ions like calcium and magnesium, 0.1% of earth's crust has manganese, soil contains 7–9000 ppm manganese [42] .Seawater as well as atmosphere also has presence of manganese. Hence manganese effect on PAM is of high research importance. Lastly iron might be present when pipes are corroded the rust formed is chemically represented as $Fe_2O_3.nH_2O(s)$ [43]. In the research work done so far to the best of our knowledge, the effect of counterions like Ca^{2+} and Mg^{2+} on thermal stability, $Mn^{2+}$and Fe^{3+} on the viscosity profile of the PAM has not been covered. These metal ions might have considerable impact on the lost circulation material's properties. Hence this thesis will investigate the effect of these counterions (Ca^{2+}, Mn^{2+}, $Mg^{2+}$and Fe^{3+}) on the viscosity, thermal stability and elastic modulus profile of PAM. The percentage total weight of solids (Polyacrylamide and Counterions) is maintained constant for all the experiments. The individual wt% of Polyacrylamide and Counterion is varied keeping the total weight of the solids in the distilled water as 1%. Additional this research will include the crosslinking of PAM with PEI in presence of manganese ions. The subsequent tables shows the sample preparation ratio's to be considered for each counterion and PAM wt%, along with the nature of the solution formed due to the addition of the counterion to the PAM solution.

The solution of PAM, counterion and distilled water mixture is prepared as per *SNF Floerger* [40], already described earlier in this thesis.

3.5.2. (a) Calcium ion (Ca^{2+})

The Table 2 shows the composition of various concentrations of polyacrylamide solution prepared with addition of calcium ion. The Calcium was obtained from Calcium Chloride 2-hydrate powder, chemically represented as $CaCl_2.2H_2O$.

Table 2: Calcium and PAM Sample preparation

PAM	$CaCl_2$	Ca^{2+}	PAM + Calcium ion	Status
gm	Gm	%	1 gm	PAM + Ca^{2+}
0.95	0.05	5	0.95gm PAM+ 0.05gm Ca	Dissolved
0.9	0.1	10	0.9gm PAM+ 0.1gm Ca	Dissolved
0.85	0.15	15	0.85gm PAM+ 0.05gm Ca	Dissolved
0.75	0.25	25	0.75gm PAM+ 0.05gm Ca	Dissolved

The total content of solids in distilled water is maintained as 1 gm. Initially the salt solution was prepared by dissolving salt and distilled water. Then Polyacrylamide powder was poured and above procedure [40] was followed. The solution was magnetically stirred to obtain a fully dissolved white colored solution without any flakes of PAM. All the concentrations prepared as per the Table 2, were fully dissolved and final color of solution was white in color.

3.5.2. (b) Magnesium (Mg^{2+})

The Table 3 shows the composition of Polyacrylamide solutions prepared with addition of Magnesium ion. The Magnesium ion was obtained from Magnesium Chloride 6-hydrate powder, chemically represented as $MgCl_2.6H_2O$.

Table 3: Magnesium and PAM sample preparation

PAM	$MgCl_2$	Mg^{2+}	PAM + Magnesium ion	Status
gm	gm	%	1 gm	PAM + Mg^{2+}
0.95	0.05	5	0.95gm PAM+ 0.05gm Mg	Dissolved
0.9	0.1	10	0.9gm PAM+ 0.1gm Mg	Dissolved
0.85	0.15	15	0.85gm PAM+ 0.05gm Mg	Dissolved
0.75	0.25	25	0.75gm PAM+ 0.05gm Mg	Dissolved

The total content of solids in distilled water is maintained as 1 gm. Initially the salt solution was prepared by dissolving salt and distilled water. Then Polyacrylamide powder was poured and above procedure [40] was followed. The solution was magnetically stirred to obtain a fully dissolved white colored solution without any flakes of PAM. All the concentrations prepared as per the Table 3, were fully dissolved and final color of solution was white in color

3.5.2. (c) Ferric ion (Fe^{3+})

The Table 4 shows the composition of various concentrations Polyacrylamide solution prepared with addition of Ferric ion. The Iron was obtained from Ferric Nitrate non-anhydrate, chemically represented as $Fe_2(NO_3)_3.9H_2O$.

Table 4: Iron and PAM sample preparation

PAM	FeN	Fe^{3+}	PAM + Iron	Status
gm	gm	%	1% gm	PAM + Fe^{3+}
0.99	0.01	1	0.99gm PAM+ 0.01gm Fe	Dissolved
0.98	0.02	2	0.98gm PAM+ 0.02gm Fe	Dissolved
0.95	0.05	5	0.95gm PAM+ 0.05gm Fe	Dissolved
0.9	0.1	10	0.9gm PAM+ 0.1gm Fe	Dissolved
0.85	0.15	15	0.85gm PAM+ 0.05gm Fe	Dissolved
0.75	0.25	25	0.75gm PAM+ 0.05gm Fe	Precipitate

The total content of solids in distilled water is maintained as 1%. Initially the salt solution was prepared by dissolving salt and distilled water. Then Polyacrylamide powder was poured and above procedure [40] was followed. Each solution of this mixture of Iron and PAM was magnetically stirred for around 48 hours to obtain a fully dissolved reddish brown colored solution without any flakes of PAM.

In the Figure 10, the PAM/Fe^{3+} (99/1%) and PAM/Fe^{3+} (99/1%) concentration samples prepared in the laboratory are shown. The solution is reddish brown and highly viscous in nature. There is no precipitate formed in the solution and PAM is completely dissolved in ferric ion solution.

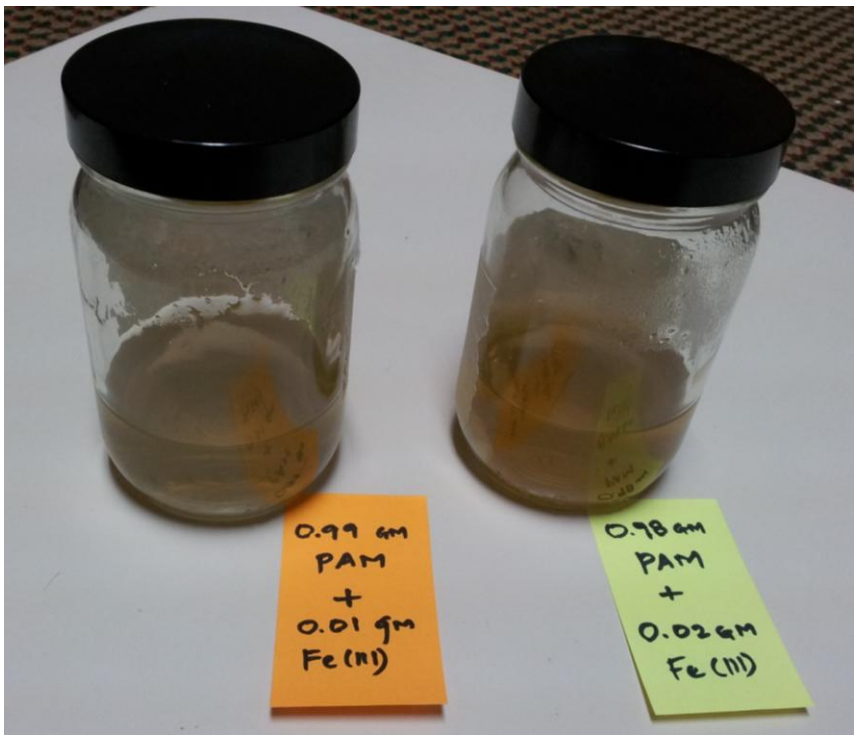

Figure 10: PAM in Iron Counterion

In the Figure 11, the PAM/Fe^{3+} (95/5%), PAM/ Fe^{3+} (90/10%) and PAM/ Fe^{3+} (85/15%) concentration samples prepared in the laboratory are shown. The solution is reddish

brown and highly viscous in nature. There is no precipitate formed in the solution and PAM is completely dissolved in ferric solution.

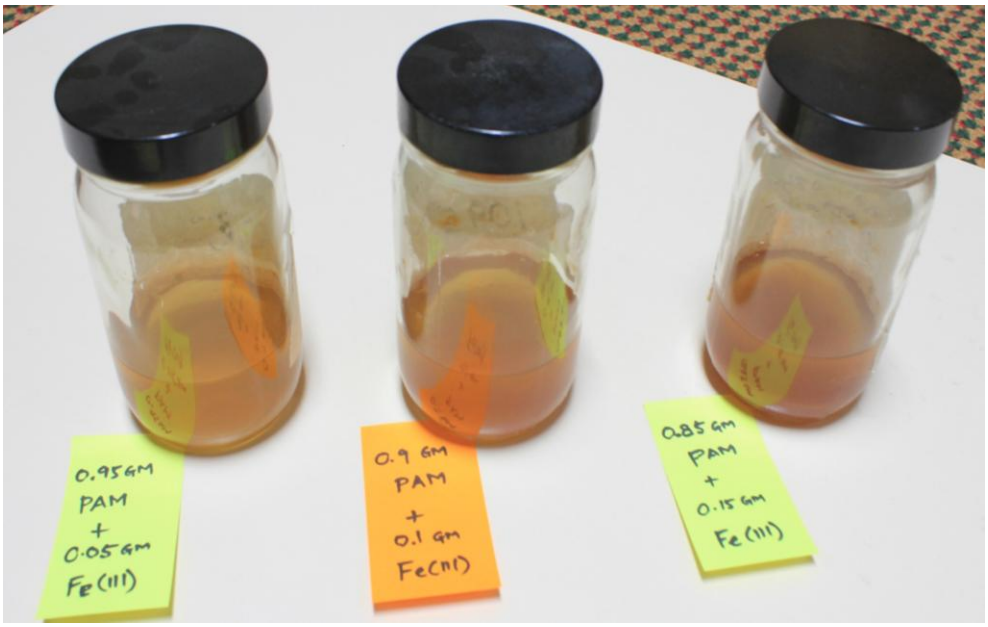

Figure 11: PAM in Iron Counterion

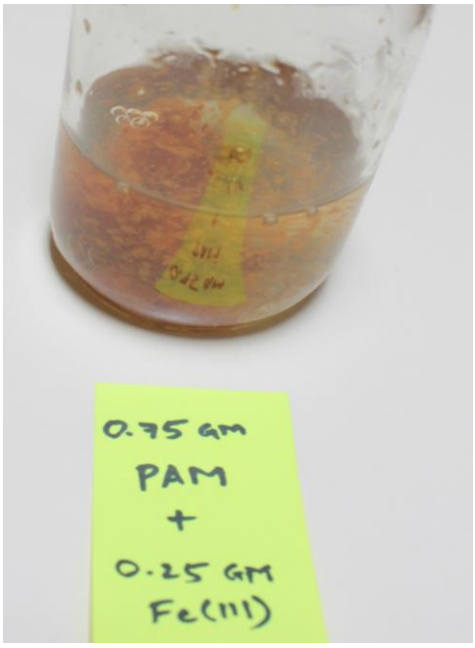

Figure 12: PAM in Iron Counterion

Higher the concentration of PAM in a solution, easier it was to dissolve the mixture. The concentration prepared as per the Table 4 in which 0.75gms of PAM was used along with 0.25gms of Fe^{3+} in distilled water could not get dissolved and a precipitate of light reddish color solution was formed. Hence the last concentration in the Table 4 was not tested for rheology effects. Figure 12, shows concentration composition PAM/Fe^{3+} (75/25%), which still has formed a precipitates with flakes of PAM still left un-dissolved. This composition was stirred on a electronic stirrer for 36 hours but still left un-dissolved. This kind of solution was unsuitable for conducting rheological measurements hence no tests were conducted on this sample.

3.5.2. (d) Manganese ion (Mn^{2+})

The Table 5, below shows the composition of various concentrations of Polyacrylamide solution prepared with addition of Manganese ion. The Manganese was obtained from Manganese Nitrate hydrate powder.

Table 5: Manganese and PAM sample preparation

PAM	**Mn_3N_2**	**Mn^{2+}**	**PAM + Manganese**	**Status**
gm	**gm**	**%**	**1% wt**	PAM + Mn^{2+}
0.95	0.05	5	0.95gm PAM+ 0.05gm Mn	Dissolved
0.9	0.1	10	0.9gm PAM+ 0.1gm Mn	Dissolved
0.85	0.15	15	0.85gm PAM+ 0.05gm Mn	Dissolved
0.75	0.25	25	0.75gm PAM+ 0.05gm Mn	Dissolved

The total content of solids in distilled water is maintained as gm. Initially the salt solution was prepared by dissolving salt and distilled water. Then Polyacrylamide powder was poured and above procedure [40] was followed. The solution was magnetically stirred to obtain a fully dissolved white colored solution without any flakes of PAM. All the

concentrations prepared as per the Table 5 were fully dissolved and final color of solution was white in color.

3.5.3 Polyacrylamide/Crosslinker/Counterion

0.95 wt % of PAM was crosslinked with 0.5 wt % of Polyethyleneimine (PEI) at 25^{o}C in presence of 0.05 wt% manganese. PEI is an organic Cross-linker added to PAM which under high temperature and pressure forms gel [44].

3.6 Experimental Set up for LCM Test

A see through experimental setup is designed for testing the sealing and blocking effectiveness of the designed LCM. The flow chart model is shown in Figure 13, initially this setup is designed to work at low temperatures and pressures.

It consists of ISCO Pump (1) to pressurize the cylinders containing Lost Circulation Material (LCM) present inside FPC Pill (2) and Drilling fluid or Drilling Mud present inside FPC Mud (3), Plexi-glass tube (4) is filled to glass beads of various sizes to simulate the formation, Mud Pit (5) is placed at the end of the setup to collect the fluid coming out of the Plexi-glass tube and the Pressure gauges (6) are arranged before and after the Plexi-glass tube to measure the drop in pressure.

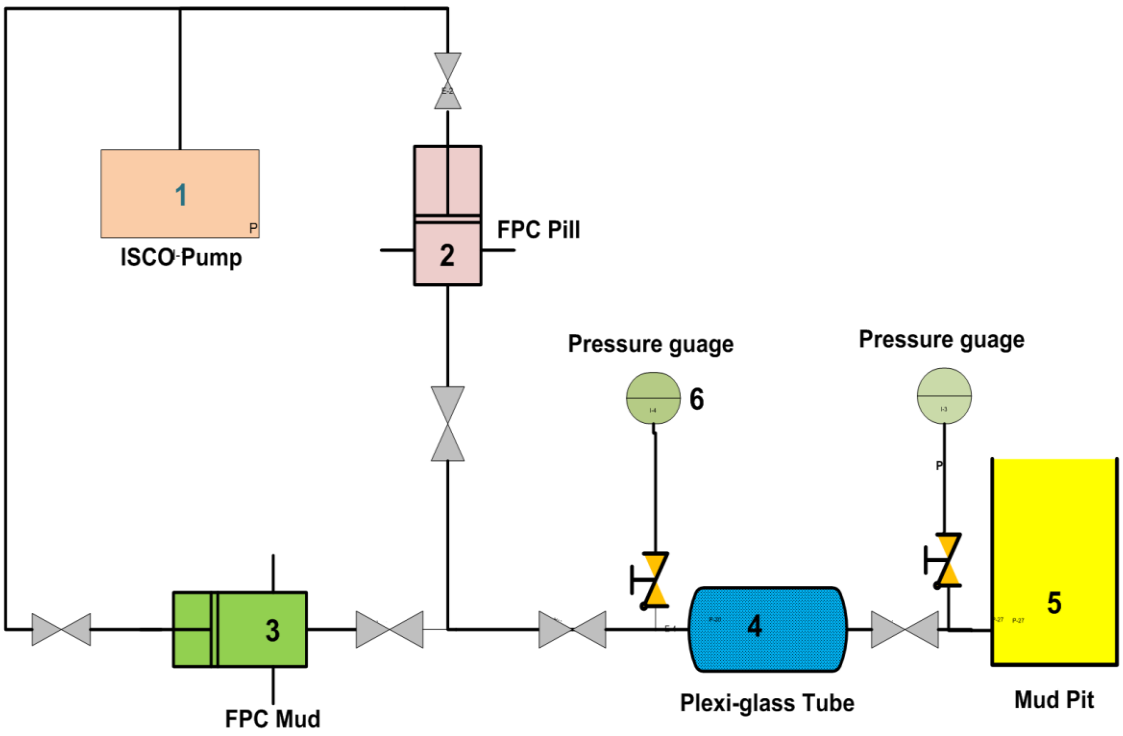

Figure 13: Design of Experimental set up for LCM test

It has been designed in such a way that the ISCO pump **(1)** pressurizes the mud and LCM pill cylinder. The Drilling mud is pumped by FPC MUD **(3)** at a rate and pressure adjusted by the operator and simultaneously the LCM will be pumped by the piston from the FPC PILL **(2),** both these fluids i.e. Drilling fluid and LCM will meet at the junction of the two valves and will get mixed, the mixture consisting of LCM and Drilling fluid will flow towards transparent Plexi-glass Cell, the Plexi-glass cell which is filled with glass beads representing the formation, with a known permeability value.

Initially in the first stage the drilling fluid alone will be passed through the Plexi-glass cell and the pressure drop, flow rate and the amount collected in the mud pit will be measured. In the second stage the drilling fluid will be mixed with the LCM and will

again passed through the plexi-glass tube and the pressure drop across the gauges, flow rate and the amount of fluid collected in the mud pit will be calculated to obtain the sealing and blocking efficiency of the LCM.

Figure 14: Experimental set up for LCM test

Figure 14, shows the model prepared for the testing of LCM, at the later stage this setup will be developed further for high temperatures and pressures testing with plexi-glass hanging on a blue stand as a main component representing formation.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Investigating Linear Viscoelasticity Region of Polyacrylamide

The region where stress and strain are related linearly is identified as Linear Viscoelastic region (LVR) region. It is the region where modulus is independent of stress or strain used. The amplitude obtained from LVR is used as an input parameter for all the subsequent tests. The behavior for any liquid is completely described by a single function of time [45]. Storage modulus G′ is plotted against percentage of strain at various concentrations. Figure 15 shows that small deformations applied slowly on the molecules of the PAM., The molecular arrangements will never go away from equilibrium state.

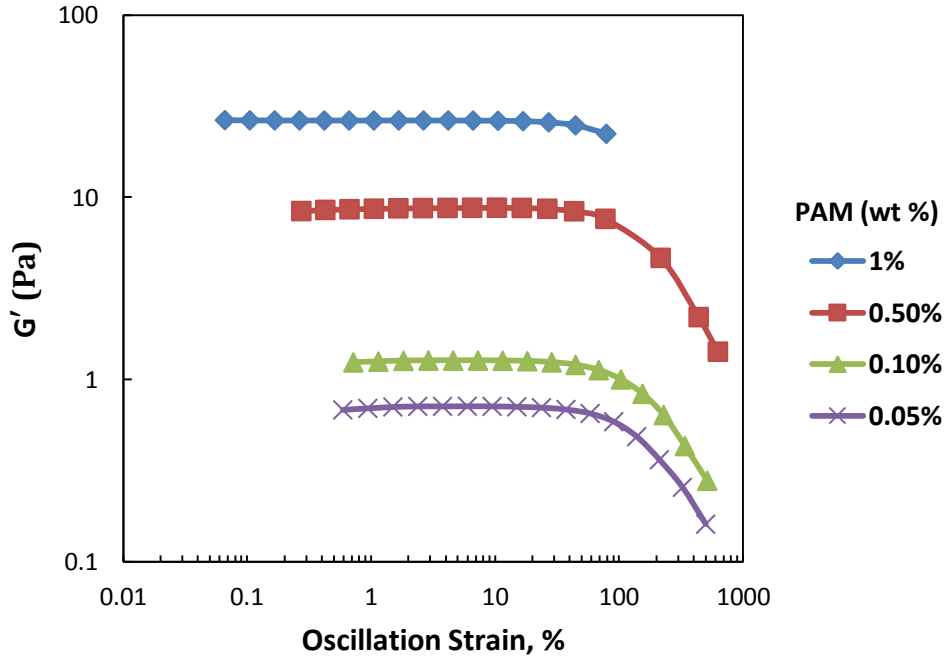

Figure 15: Linear Viscoelastic region of PAM

For 1 wt % PAM, the LVR is observed upto 16.92% strain, as the concentration is decreased to 0.5, 0.1 and 0.05 wt % the straight line deviates at 43.4, 68.52 and 90.53%, respectively. Hence it has been observed that approximately at around 15% strain all the concentrations of PAM are within the LVR domain.

The Figure 16 is a plot between Loss Modulus G″ and the strain applied on the PAM solution. For 1 wt % PAM, the G″ is unaffected upto 78.92% strain, as the concentration is decreased to 0.5, 0.1 and 0.05 wt % the straight line deviates at 16.826, 103.52 and 138.53%, respectively. Hence it has been observed that approximately at around 10-15% strain G″ at all the concentrations of PAM are within the LVR domain.

These measurements of G′ and G″ at LVR domain will bridge the gap between the molecular structure and product performance [36] as both G′ and G″ represent the gel strength and contain structural information. If G′ is more in a solution, then the solution will behave in a elastic manner whereas if G″ is greater the solution will behave in a viscous manner. Therefore all these factors will help in designing a LCM.

Figure 17, shows the variation of the storage and loss modulus of PAM values at zero strain. As the concentration of the PAM is increased from 0.05, 0.1, 0.5 and 1 wt% the G_o' values are 0.68, 1.24, 8.41, 26.52 Pa respectively. Similarly the G_o'' values at same concentrations are 0.4, 0.65, 3.19 and 8.35 Pa respectively. Hence from Figure 17, it can be concluded that at all the concentrations from 0.05 to 1 wt% the G_o' values are greater than G_o'', which means that elastic component is stronger than the viscous component when no strain is applied.

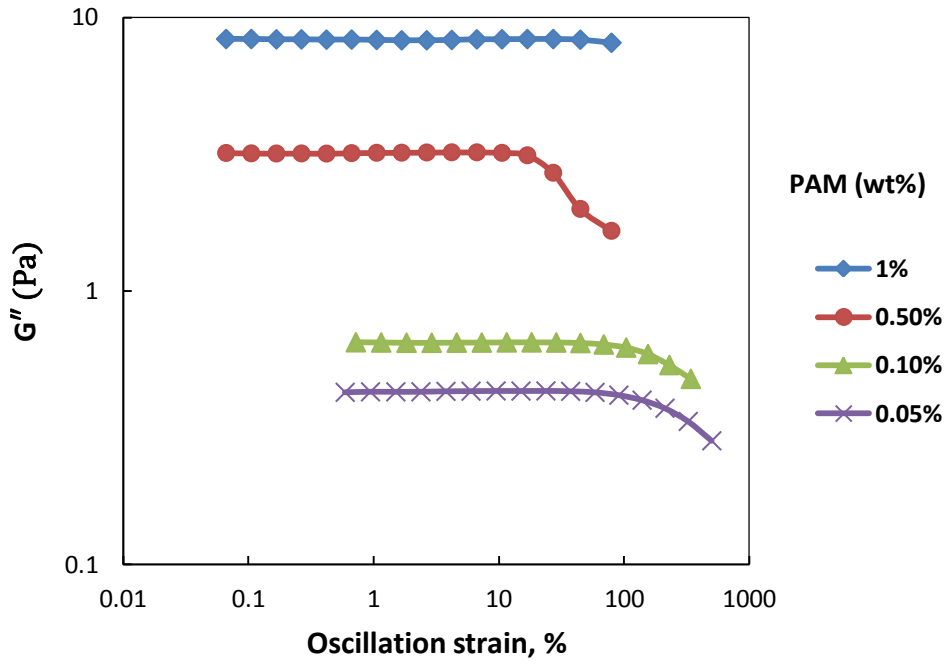

Figure 16: Effect of Strain on Loss Modulus of PAM

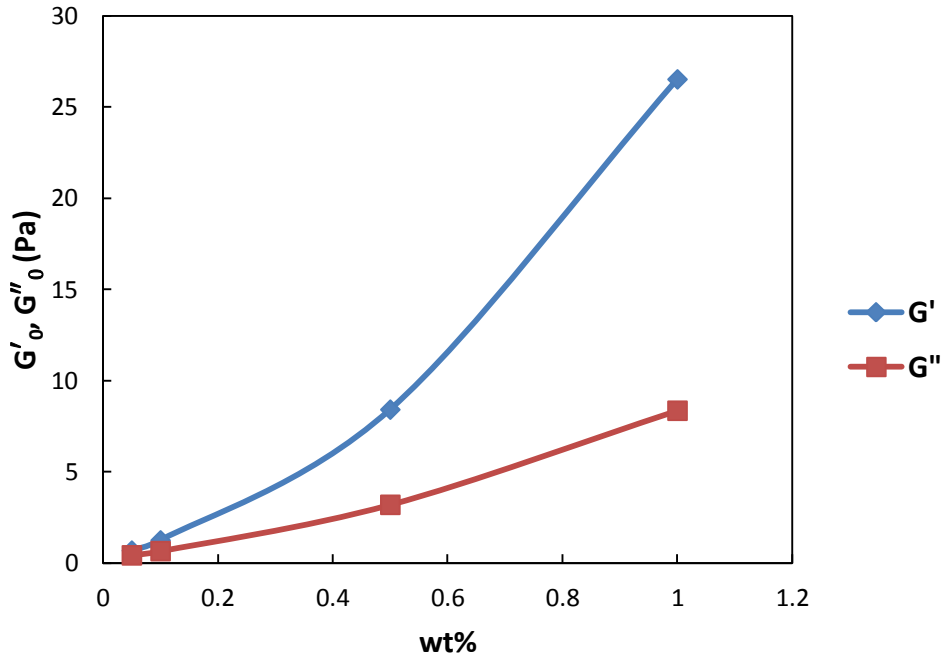

Figure 17: Variation of Storage and Loss Modulus at Zero Strain

4.2 Rheology of Polyacrylamide

To study the effect of shear rate on the viscosity profile of the PAM, flow sweep test was conducted to obtain the relationship. The Figure 18 shows behavior of the viscosity with varying shear rate. The viscosity of the PAM solution is decreasing with reduction in PAM concentration from 0.05 to 1 wt %.

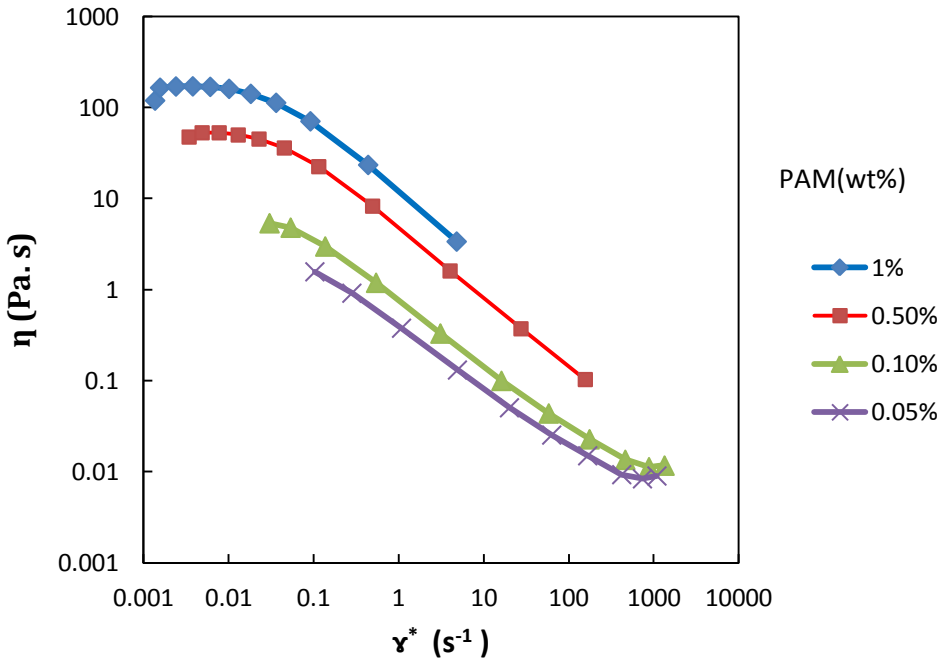

Figure 18: Effect of Shear rate on Viscosity of PAM

It is observed that for every reduction in the concentration of PAM by 50% there is almost 30-50% reduction in the actual viscosity of PAM at respective shear rate. The Polymer exhibits a shear thinning behaviour.

The zero rate viscosities of the PAM were measured at zero shear rate. Carreau model was fit on the plot of η v/s γ^* to obtain zero rate viscosity for a particular concentration of PAM to understand the effect of concentration.

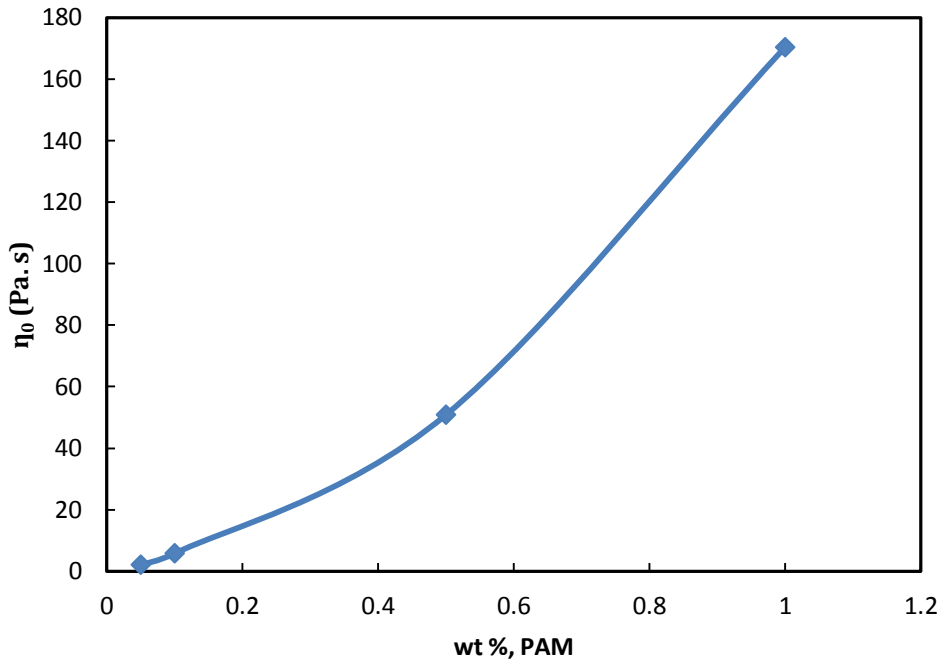

Figure 19: Effect of PAM concentration on viscosity at zero shear rate.

From the Figure 19, η_o is increasing as the concentration of the PAM is increasing from 0.05 to 1 wt % PAM. For the PAM concentrations of 0.05, 0.1, 0.5 and 1% by wt the zero rate viscosities are 2.11, 5.84, 50.88, and 170.375 Pa.s, respectively. This might be due to concentration, molecules and network structure of the PAM. Higher the concentration of PAM, better is the viscosity, which means that Viscosity is directly proportional to the concentration of Polymer.

Figures 20 and 21 show the effect of angular velocity on the dynamic viscosity profile of the PAM solution. The Dynamic viscosity is decreasing with increase in angular frequency for all concentrations of PAM solutions from 0.05% - 1% prepared upto 500 rad/s providing a shear thinning behaviour. The reduction of dynamic viscosity can be

attributed to the role decreasing PAM concentration, molecules and consequent network behaviour of the PAM.

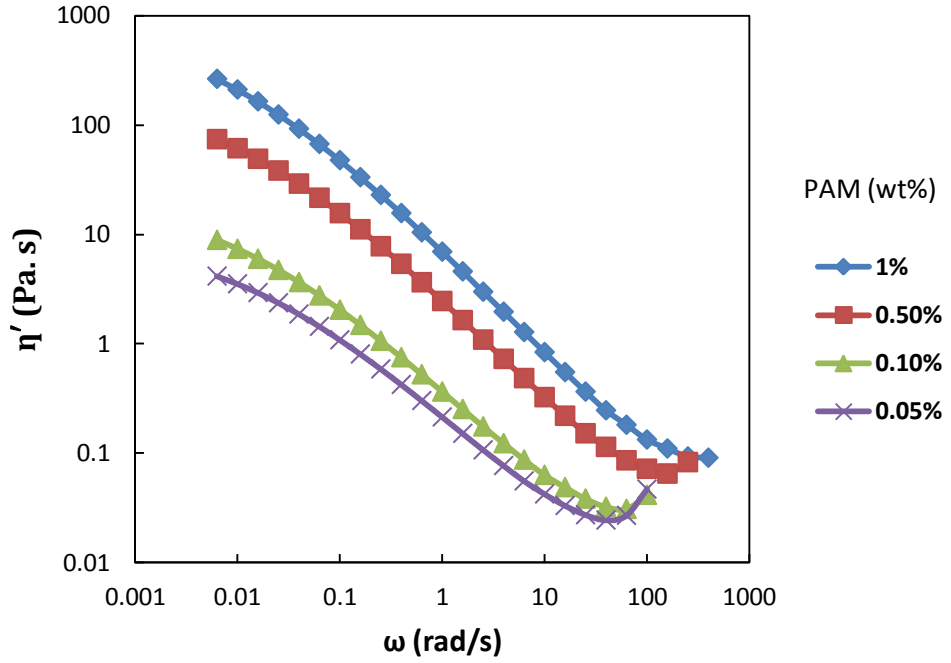

Figure 20: Effect of angular velocity on dynamic viscosity of PAM

For 1 wt % PAM solution, as shown in Figures 20, the dynamic viscosity 263 Pa.s and out of phase component of viscosity in Figure 21, 170 Pa.s at an angular velocity of 0.00628 rad/s are decreasing to dynamic viscosity of 0.0906 Pa.s and out of phase component of viscosity in Figure 21, 0.08 Pa.s at an angular velocity of 396 rad/s. At low angular velocity of 0.00628 rad/s as we decreased the concentration of the PAM solution to 0.5, 0.1 and 0.05 wt % the dynamic viscosity reduced to 74, 8.89 and 4.14 Pa.s respectively and the out of phase components of viscosities at 0.5% wt, 0.1% and 0.05% wt were 37.87, 4.17, and 1.51 Pa.s. Hence PAM concentration has large impact on the dynamic viscosity and out of phase component of the solution.

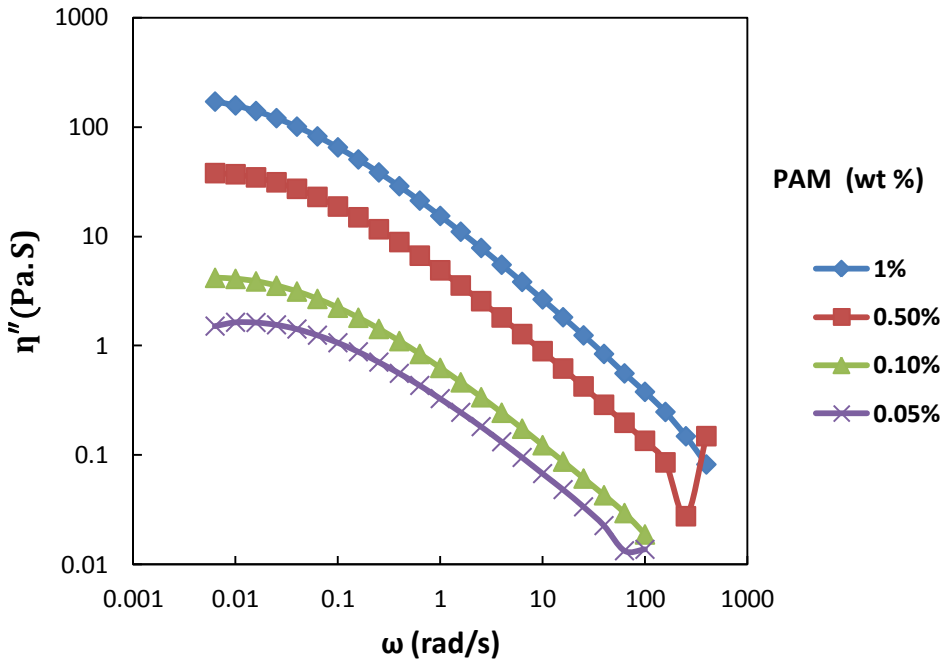

Figure 21: Effect of angular velocity on out of phase component of viscosity of PAM

At higher angular velocities of over 50 rad/s, it has been observed that for the concentration 1, 0.5, 0.1 and 0.05 wt % the dynamic viscosities are 0.09, 0.08, 0.06 and 0.04 Pa.s, respectively and for same concentration the values of out of phase component of viscosities are 0.08, 0.14, 0.018 and 0.01 Pa.s respectively. All the values of dynamic viscosity and out of phase component of viscosity are approaching close to each other and become almost equal at high angular velocities of over 50 rad/s, this is due to the fact that at high frequency, the effect of frequency is more prominent as compared to effect of material properties like dynamic viscosity, out of phase component of viscosity, due this fact at 396 rad/s the last data point in a concentration of 0.5 wt% jumps to 0.14 Pa, which should be neglected. Hence the true response of material/PAM can only be observed at low frequency.

Viscoelastic properties like G′, G″ define gel strength and represent structural information of the compound. Hence these parameters are important to design gel formulations depending upon requirements. The effect of frequency sweep on the loss and storage modulus of the PAM solution as a function of concentration is observed from the Figure 22 and 23. It has been observed that both G′, G″ gradually increase with PAM concentration and frequency sweep. The storage modulus of the PAM solution with concentrations from 0.05, 0.1, 0.5 and 1 wt % are at an angular velocity of 0.0628 rad/s are 0.009, 0.023, 0.23 and 1.07 Pa respectively. Also it has been observed that for both 0.05 wt % PAM and 0.1 wt % PAM the G′ values are almost equal and that the slope of both these curves also is the same.

From Figure 23, loss modulus of the PAM solution with concentrations from 0.05, 0.1, 0.5 and 1 wt % are at an angular velocity of 0.0628 rad/s are 0.026, 0.055, 0.46 and 1.65 Pa, respectively. Also it has been observed that for both 0.05% wt PAM and 0.1% wt PAM the G″ values are almost equal and that the slope of both these curves also is the same.

From the Figures 22 and 23, Loss modulus G″ has higher values than storage elastic modulus G′, which means that viscous component is stronger than the viscous component.

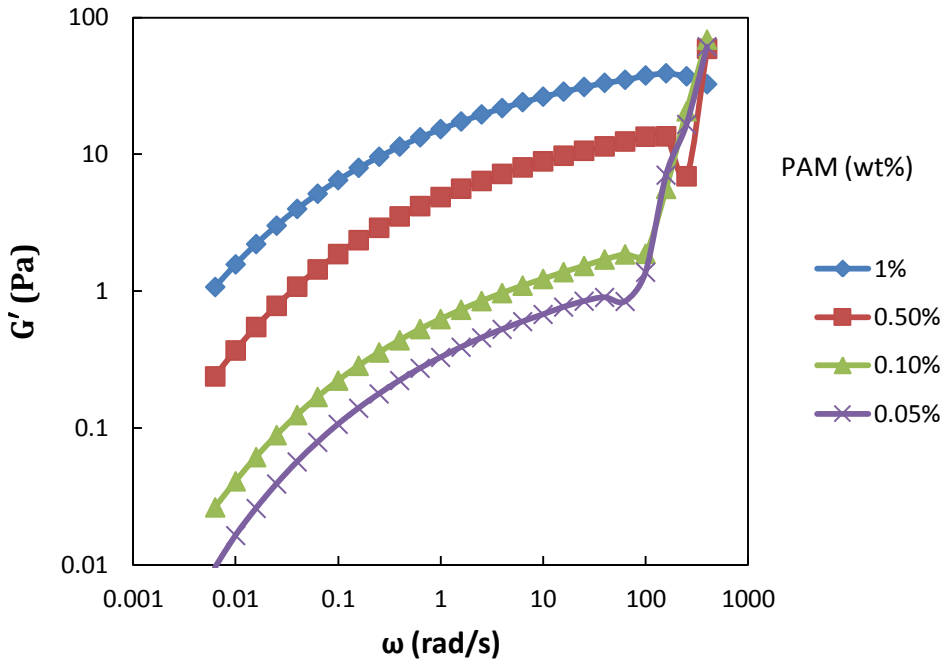

Figure 22: Effect of angular velocity on Storage modulus of PAM

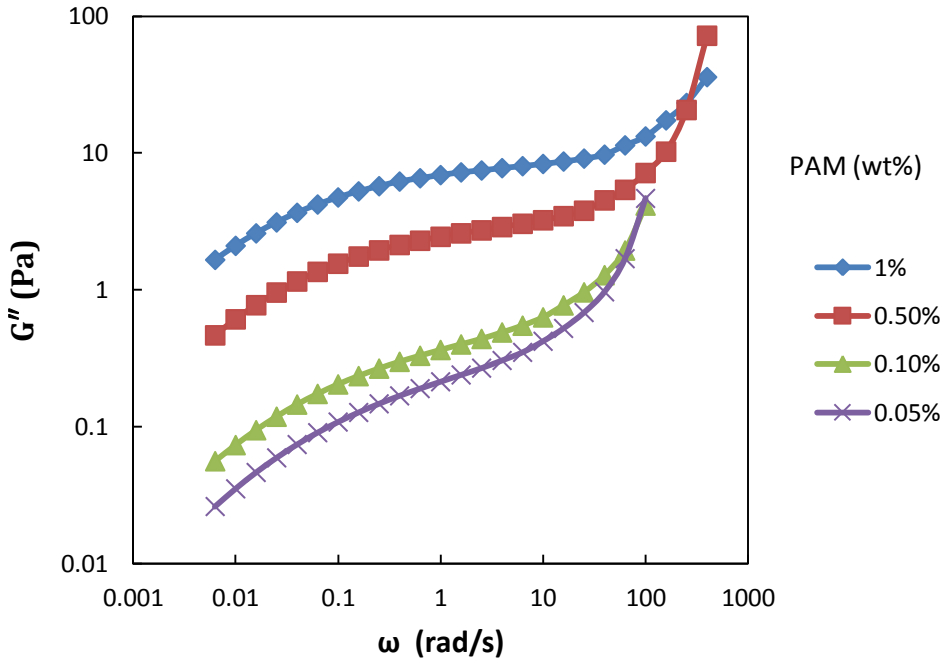

Figure 23: Effect of angular velocity on loss modulus of PAM

At high angular velocities of over 50 rad/s it is observed that, storage modulus and loss modulus at all the concentrations of PAM become almost equal. G′ and G″ at all concentrations become almost same at a very high frequency because at high angular velocities the effect of frequency is more prominent as compared to effect of material properties like temperature, concentration, modulus of elasticity, loss and storage modulus etc.

Hence the true response of material/PAM can only be observed at low frequency as the effect of materials is more prominent and it can also be concluded that as 0.05 wt % PAM will have same effect as 0.1 wt % PAM and for future application, inorder to save costs, 0.05 wt % PAM can be used in place of 0.1 wt % PAM. Also, it has been observed that for both 0.05 wt % PAM and 0.1 wt % PAM the G″ values are almost equal and that the slope of both these curves also is the same. Hence it can be concluded that for low concentrated PAM solutions, the viscosity reduction rate is almost equal. All the concentrations of the PAM exhibit shear thinning behavior.

For lost circulation agents, thermal stability is a very important criteria as in downhole the seal formed by the lost circulation materials has to withstand very high temperatures of formations. Initially a sample used *Flopaam 3330s* with stability as 70^{o}C as mentioned by the manufacturer as selected for the experiments. The PAM was tested for its stability at 70^{o}C for various concentrations.

The Figure 24 and 25 shows G′ and G″ measured at room temperature 25^{o} C and subsequently inorder to test its temperature withstanding ability.

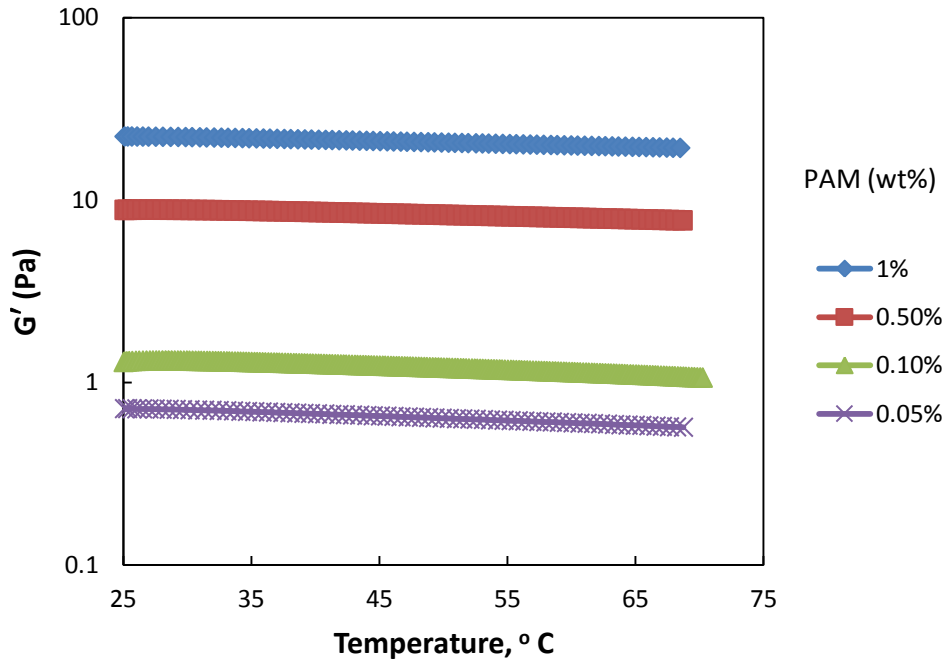

Figure 24: Effect of Temperature on storage modulus of PAM

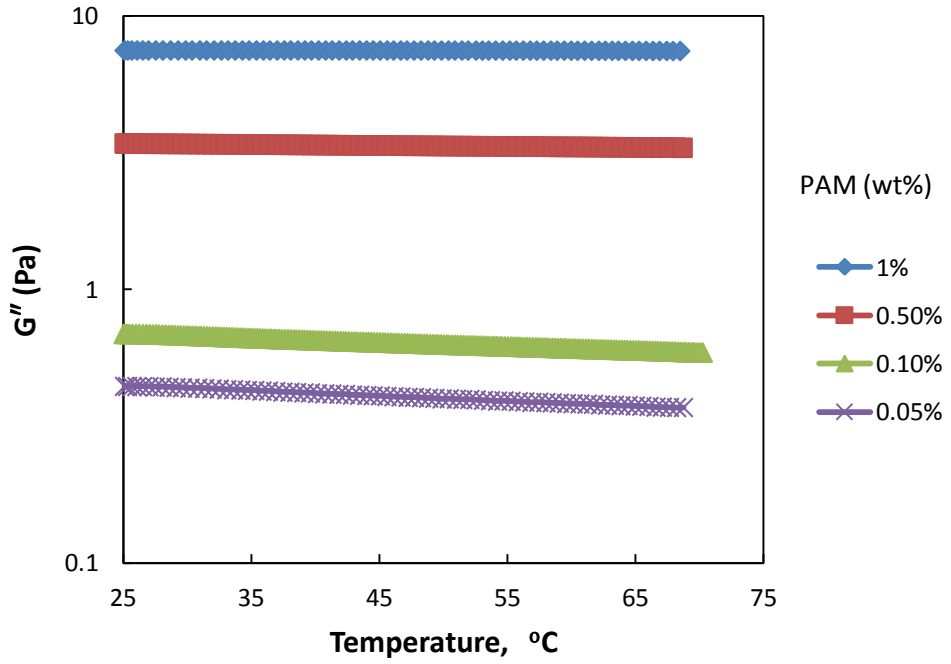

Figure 25: Effect of Temperature on Loss Modulus of PAM

The temperature was increased in short intervals upto 70^{o} C. Both G′ and G″ are straight lines for all the concentrations of PAM solution. There is hardly any deviation of the points from the straight line at all the temperatures upto 70^{o} C. The graph suggests that exposure to the temperature of 70^{o} C is not affecting the properties of the polyacrylamide. The loss and storage modulus of all concentrations of the PAM solution remain same at a temperature range of 25-70^{o}C.

Hence it can be concluded from the values of the loss and storage modulus or the energy stored inside the pure PAM solution with *Flopaam* sample no# 3330S at all concentrations starting from lowest 0.05 to 1 wt % is thermally stable at 70^{o}C without any appreciable degradation to the molecular structure

4.3 Effect of Counterions on viscosity profile of PAM

Polyacrylamide is a very important constituent [5, 7, 15, 18, and 19] of most of the lost circulations materials. Inorder to increase gel strength, stability, to reduce the cost of material by adding a relatively lower cost ion which can enhance its viscosity crosslinkers are added. The effect of counterions like Cr^{+3}, Al^{+3}, Zr^{+4} [46], Hydroquinone (HQ) [47] for improving mechanical strength, Chromium acetate [14 and 48] for improving gel strength and water-N, N dimethylformamide [49] on polyacrylamide was studied. Chromium was used as a cross-linker for improving gel strength, mechanical strength, stability [14, 46 and 48].

The PAM undergoes the following hydrolysis reaction as shown in Figure 26, the reaction is very fast initially due to neighbor amide group catalytic effect and as the reaction proceeds it become slow due to columbic repulsion between negative charges of

carboxylate groups on the polymer chain and hydroxide ions. Partially hydrolyzed PAM is a polyelectrolyte with negative charges on the carboxylate groups, hence there are strong interactions between polymer chains and cations [50].

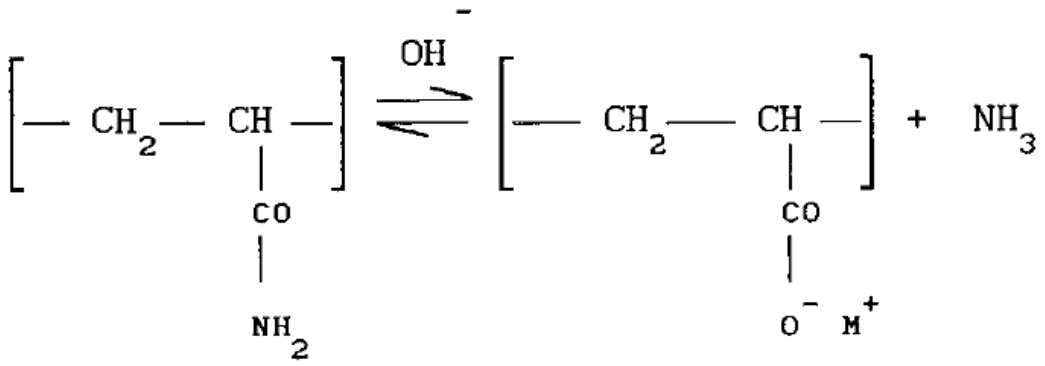

Figure 26: PAM reaction with Cations [50]

M^{+} denotes Cations, X and Y are the numbers of carboxylate and amide groups, respectively. Effect of Calcium and magnesium on viscosity profile of PAM was studied earlier [51], but its effect on the thermal stability and elastic modulus was not covered as far as our knowledge is concerned. This research thesis focuses mainly on studying the impact of these Ca^{+2}, Mg^{+2}, Mn^{+2} andFe^{+3} counterions on viscosity profile of PAM. Calcium, Magnesium, Manganese and Iron were individually mixed with PAM in presence of distilled water and the effect counter-ions on elastic modulus, viscous modulus, viscosity and thermal stability of the PAM was studied. The following are the results obtained after studying the effect of counterions on PAM.

4.3.1 Calcium (Ca^{2+})

To study the effect of shear rate on the viscosity profile of the PAM in presence of calcium ion, flow sweep test was conducted to obtain the relationship. The Figure 27 shows behavior of the viscosity with varying shear rate.

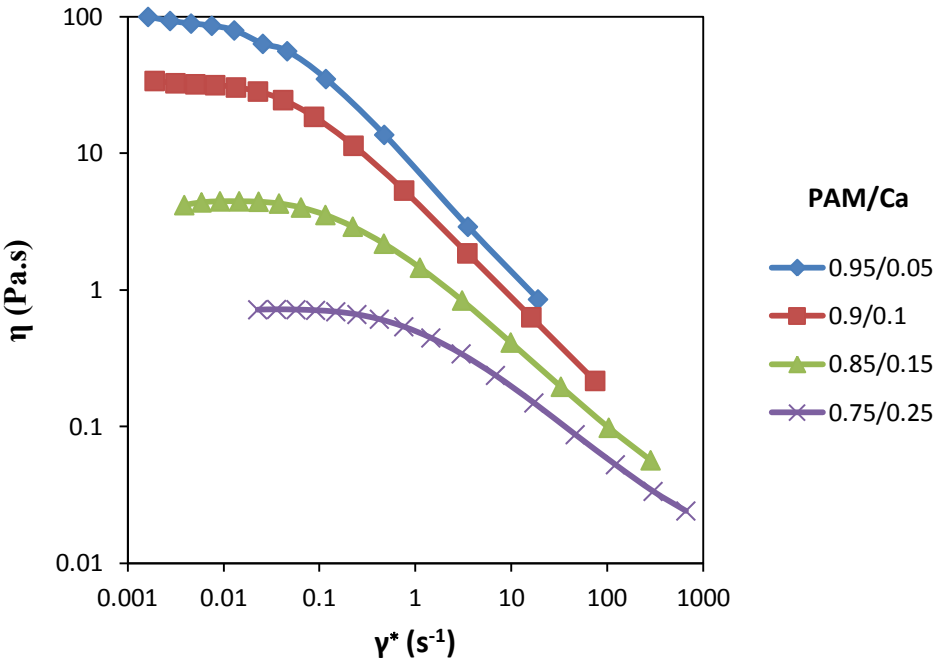

Figure 27: Effect of Shear rate on viscosity of [PAM/Ca] Solution

The viscosity of the Polyacrylamide in presence of calcium ion solution is decreasing with reduction in weight of the PAM from 0.95 g to 0.75 g and increase in weight of calcium ions from 0.05 g to 0.25 g. For 0.05 g weight reduction in PAM and 5% increase in weight of calcium ions from previous concentration, there is almost 30-50% reduction in the actual viscosity of PAM at respective shear rate

The zero shear rate viscosity of PAM/Ca was calculated using Carreau model. These η_o were plotted against concentration of the calcium to study its impact.

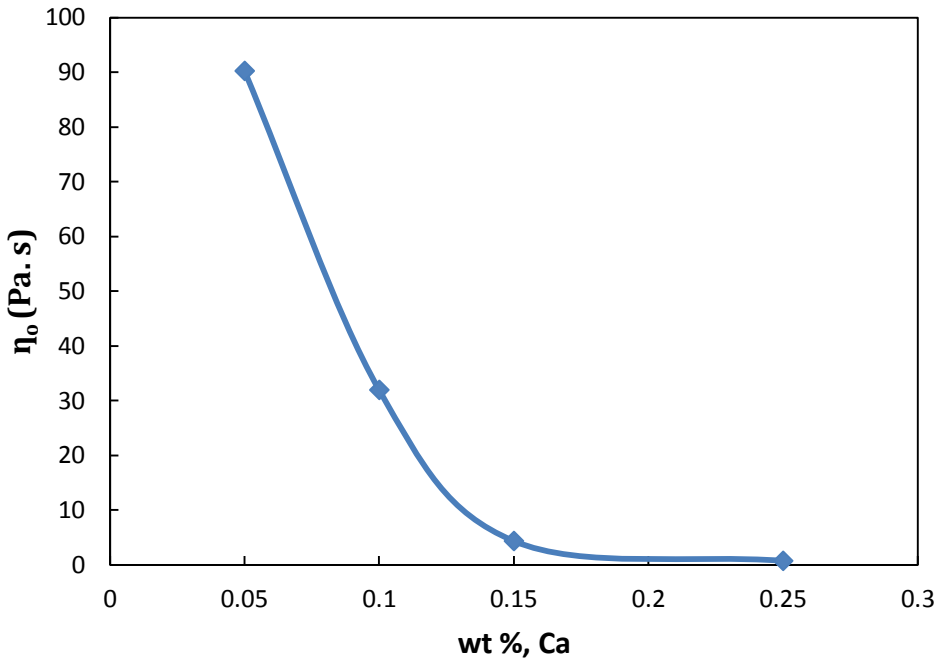

Figure 28: Effect of Calcium ion on viscosity of PAM at zero shear rate

From the Figure 28, it is observed that, η_o is decreasing as the ratio of weight of the PAM is decreasing from 0.95 to 0.75 PAM and simultaneously the ratio of calcium ions concentrations is increasing in 1% solids. For the concentrations 0.05, 0.1, 0.15 and 0.25 wt% increases in calcium ion, the zero rate viscosities are 90.25, 31.98, 4.32, and 0.70 Pa.s, respectively. This is due to concentration, molecules and network structure of the partially hydrolyzed PAM. It is a polyelectrolyte with negative charges on the carboxylate groups, hence there are strong interactions between polymer chains and calcium ions (cations), causing repulsions between carboxylate anions to decrease thereby reducing the chains, and hence the viscosity is reduced.

The effect of frequency sweep on the loss and storage modulus of the PAM in a calcium ion solution as a function of concentration is observed from the Figure 29.

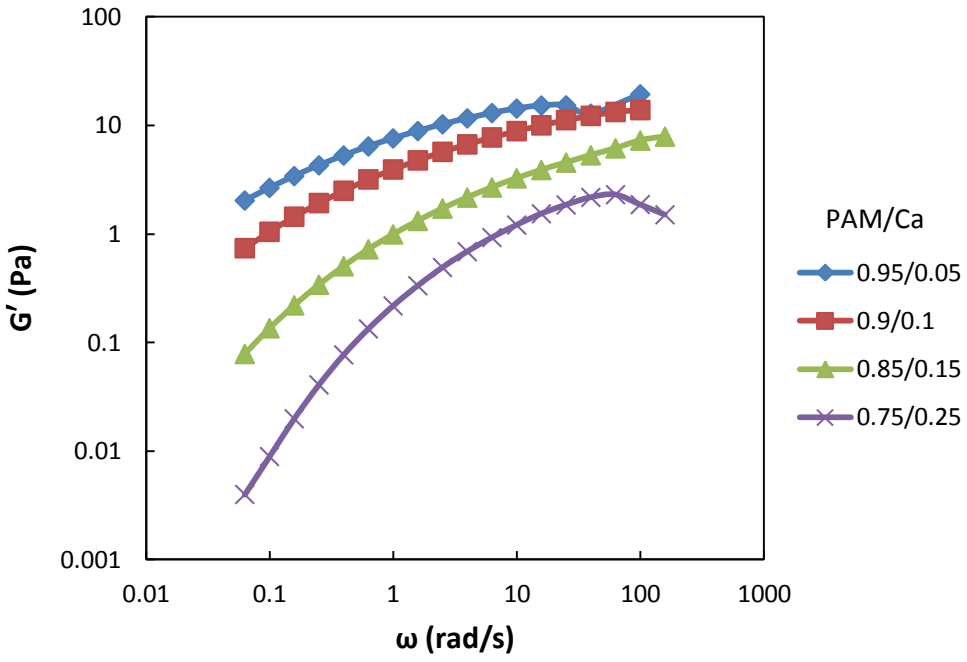

Figure 29: Effect of angular velocity on storage modulus of [PAM/Ca] solution

As the frequency increases, it has been observed that both G″ and G′ gradually increase for a particular concentration. Also it has been observed that with decrease in ratio of PAM weight and increase in calcium ion concentration in the solution both the loss and storage modulus decreases. The storage modulus of weight ratios of (PAM/Ca) solutions with concentrations (0.95/0.05, 0.9/0.1, 0.85/0.15, 0.75/0.25) at an angular velocity of 0.0628 rad/s are 2.03, 0.739, 0.07 and 0.003 Pa, respectively. Also it has been observed that for weight ratios of (PAM/Ca) solution (0.95/0.05) and (0.9/0.1) the G′ values are almost equal and that the slope of both these curves also is the same.

From Figure 30, The loss modulus of weight ratio of (PAM/Ca) solutions with concentrations (0.95/0.05, 0.9/0.1, 0.85/0.15, 0.75/0.25), at an angular velocity of 0.0628 rad/s are 2.07, 1.03, 0.228 and 0.045 Pa, respectively and it has been observed that for

weight ratios (0.95/0.05 and 0.9/0.1) of (PAM/Ca), the G′ values are almost equal and that the slope of both these curves also is the same.

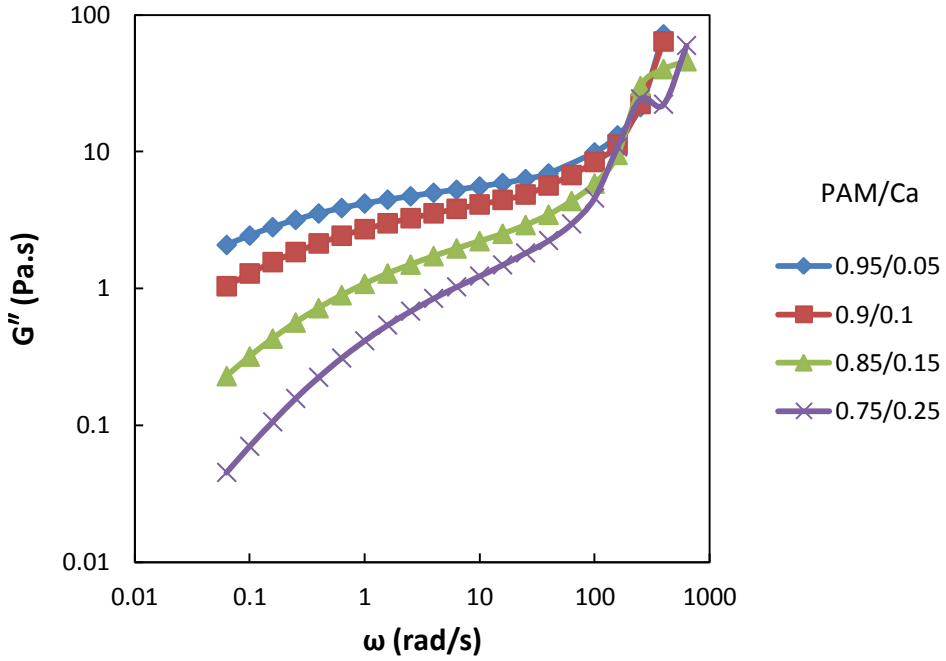

Figure 30: Effect of angular velocity on loss modulus of [PAM/Ca] solution

From the Figures 29 and 30, for (PAM/Ca) solutions with concentrations (0.9/0.1, 0.85/0.15 and 0.75/0.25), the loss modulus (G″) increases more rapidly than storage elastic modulus (G′), which means that viscous component is stronger than the elastic component whereas for (PAM/Ca) solution with concentration (0.95/0.05) the storage modulus (G″) increases more rapidly than loss elastic modulus (G′), which means that elastic component is stronger than the viscous component. At high angular velocities of over 50 rad/s it is observed that, storage modulus and loss modulus at all the concentrations of PAM in presence of calcium ion become almost equal because at high angular velocities the effect of frequency is more prominent as compared to effect of

material properties like temperature, concentration, modulus of elasticity, loss and storage modulus. Due to this reason the last data point in [PAM/Ca] solution with weight ratio [0.75/0.25] behaves in a abnormal manner as the frequency is high. Hence the true response of material/PAM can only be observed at low frequency as the effect of materials is more prominent.

Figures 31 and 32 show the effect of angular velocity on the dynamic viscosity profile of the PAM in presence of calcium ions. The dynamic viscosity is decreasing with increase in angular frequency for all concentrations of (PAM/Ca) solutions with ratios (0.95/0.05, 0.9/0.1, 0.85/0.15, 0.75/0.25), upto 500 rad/s providing a shear thinning behaviour and the gel disintegrates at high shear rates and thus it can pass through porous media with less rupture to the chemical structure.

For a mixture of PAM/Ca (0.95/Ca), the dynamic viscosity 33.07 Pa.s and out of phase component of viscosity is 32.32 Pa.s at 0.00628 rad/s are decreasing to dynamic viscosity of 0.046 Pa.s and out of phase component of viscosity is 0.08 Pa.s at of 396 rad/s. At low angular velocity of 0.00628 rad/s, for a 1 wt % of solids in water, as we decreased the ratio of PAM concentration in the solution and simultaneously increased the calcium ions wt % for a range of mixtures for all concentrations of (PAM/Ca) solutions with ratios (0.9/0.1, 0.85/0.15, 0.75/0.25), the dynamic viscosities were reduced to 16.51, 3.6 and 0.719 Pa.s, respectively and the out of phase components of viscosities at same concentrations were 11.32, 1.24, and 0.06 Pa.s.

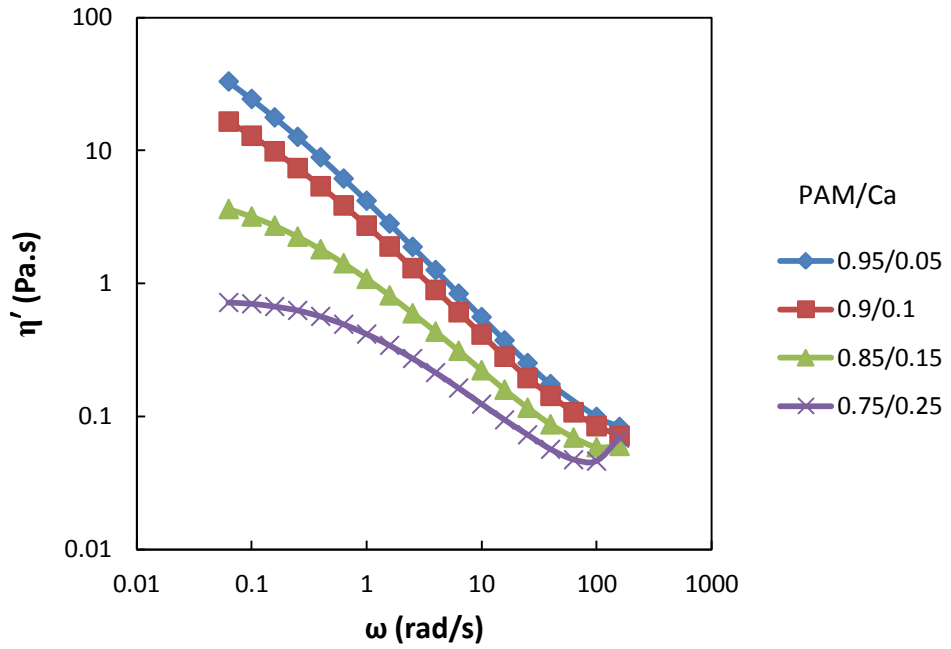

Figure 31: Effect of angular velocity on dynamic viscosity of [PAM/Ca] solution

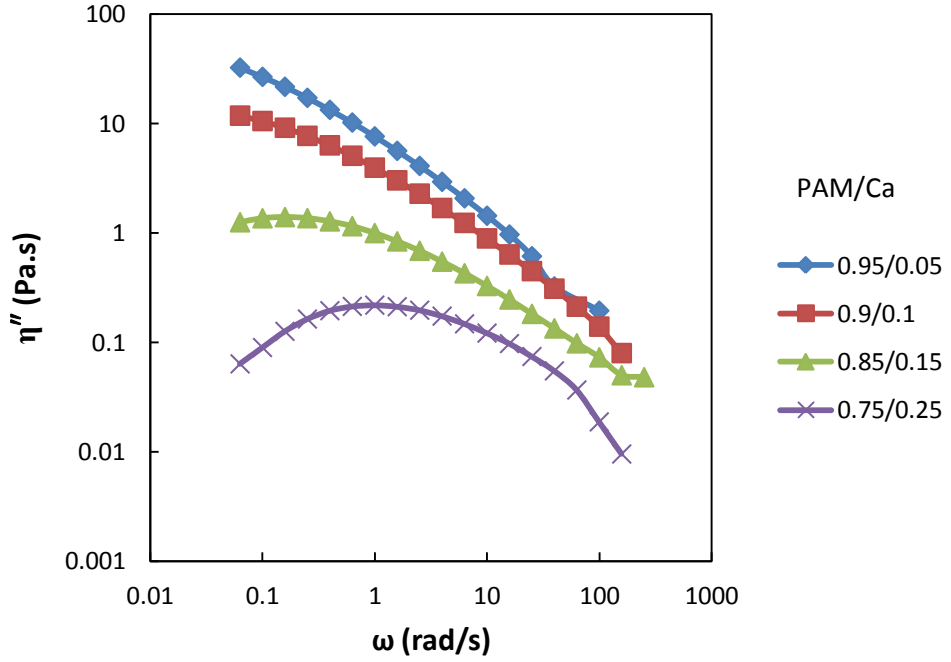

Figure 32: Effect of angular velocity on out of phase component of viscosity of [PAM/Ca] solution

Hence the addition of calcium ions has a considerable impact on the dynamic viscosity and out of phase component of the PAM.

At higher angular velocities of over 50 rad/s, it has been observed that for all the concentration the dynamic viscosities and out of phase component of viscosities are almost equal. All the values of dynamic viscosity and out of phase component of viscosity are approaching close to each other and become almost equal at high angular velocities of over 50 rad/s, this is due to the fact that at high frequency, the effect of frequency is more prominent as compared to effect of material properties like dynamic viscosity, out of phase component of viscosity etc. Hence the true response of material/PAM can only be observed at low frequency.

For lost circulation agents, thermal stability is a very important criteria as in downhole the seal formed by the lost circulation materials has to withstand very high temperatures of formations. Sample used was *Flopaam 3330s* and the thermal stability according to the manufacturer is around 70^{o}C. Hence, the PAM needs to be tested for its stability at various concentrations to check if concentration is having any impact on thermal stability. In the earlier cases (Figure 24 and 25) the pure PAM solution was thermally stable at all the concentrations. Now the effect of counterions on the thermal stability of the PAM is being tested. Figures 33 and 34 show the effect of increase in temperature on G' and G'', both G' and G'' are almost straight lines for concentrations consisting of PAM/Ca weight ratios (0.95/0.05 and 0.9/0.1). There is hardly any deviation of the points from the straight line at all the temperatures for these two mixtures upto 70^{o} C. The graph suggests that exposure to the temperature of 70^{0}C is not affecting the properties of the polyacrylamide for small concentrations of 0.05% and 0.1% wt calcium

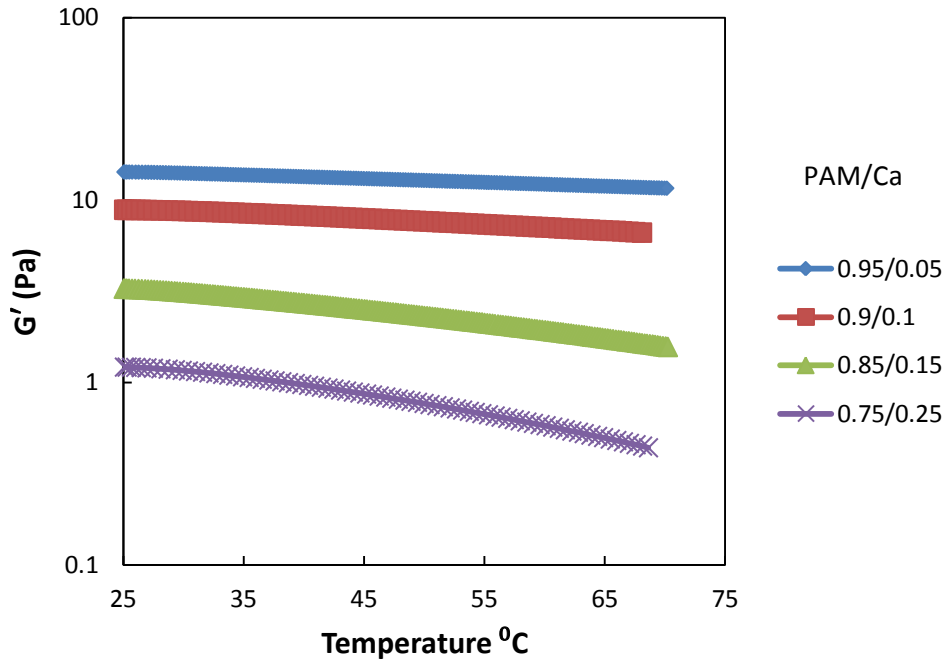

Figure 33: Effect of temperature on storage modulus of [PAM/Ca] solution

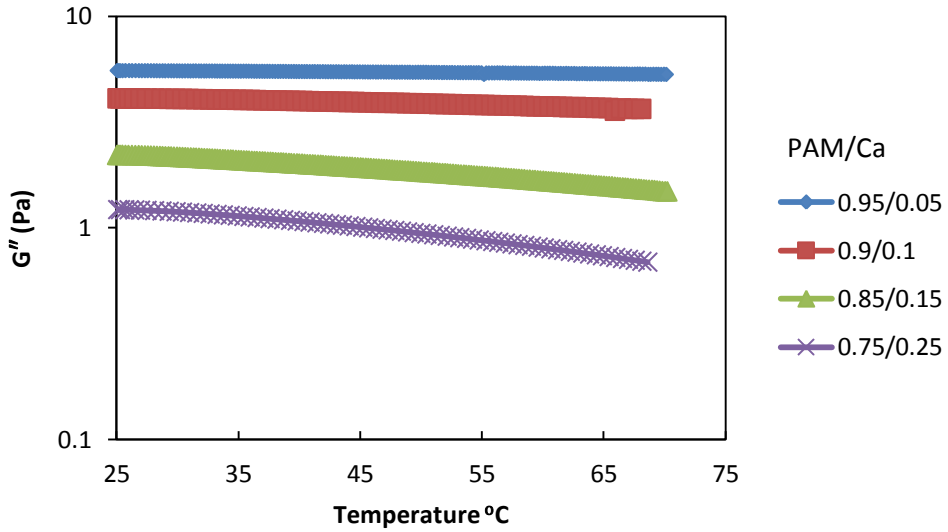

Figure 34: Effect of temperature on loss modulus of [PAM/Ca] solution

but for the increase in the calcium ion concentrations to 0.15 wt % and 0.25 wt % the stability of the PAM is decreasing from 70^{o}C to around 54^{o}C and 48^{o}C. Hence it can be

concluded from the values of the loss and storage modulus or the energy stored inside the pure PAM solution with sample *Flopaam 3330S*, that as the concentrations of the calcium increases from 0.1% wt to 0.15% wt the thermal stability is decreasing by 15^{o}C

4.3.2 Magnesium (Mg^{2+})

To study the effect of shear rate on the viscosity profile of the PAM in presence of magnesium ion, flow sweep test was conducted to obtain the relationship. The Figure 35, shows behavior of the viscosity with varying shear rate.

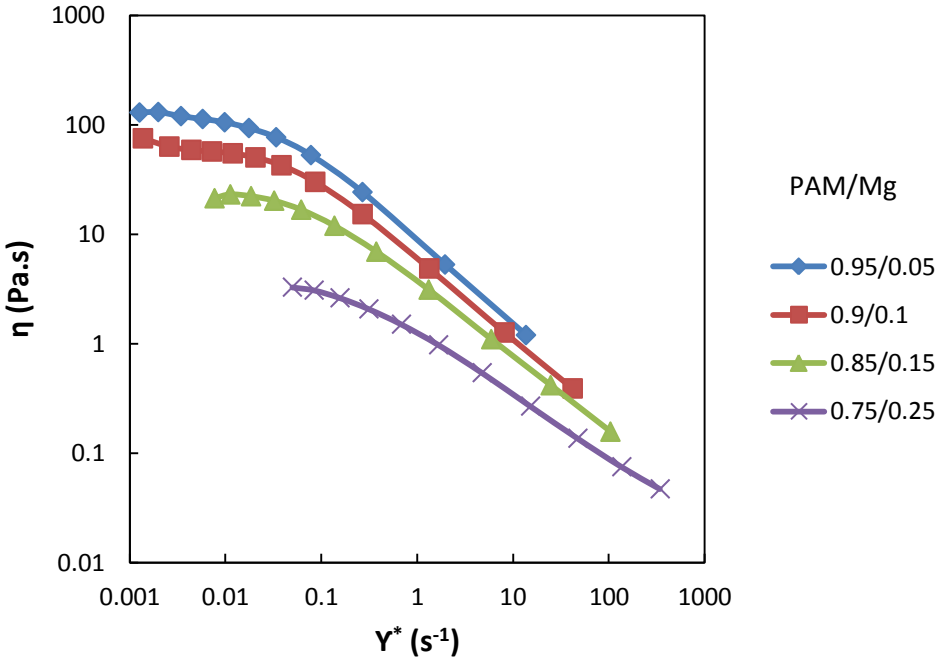

Figure 35: Effect of shear rate on viscosity of [PAM/Mg] solution

The viscosity of the Polyacrylamide in presence of magnesium ion solution is decreasing with reduction in weight of the PAM from 0.95% to 0.75 % and increase in weight of magnesium ions from 0.05 % to 0.25 % simultaneously. For 0.05 % weight reduction in

PAM and 5 % increase in weight of magnesium ions from previous concentration, there is almost 30 % in the actual viscosity of PAM at respective shear rate

The viscosity of the PAM in presence of magnesium ion was measured at zero shear rate, hence these viscosities measured are termed as zero rate viscosities. Carreau model was fit on the plot of η v/s γ to obtain zero rate viscosity for a particular concentration of PAM and magnesium ion. These η_o were plotted against concentration of the magnesium to study its impact.

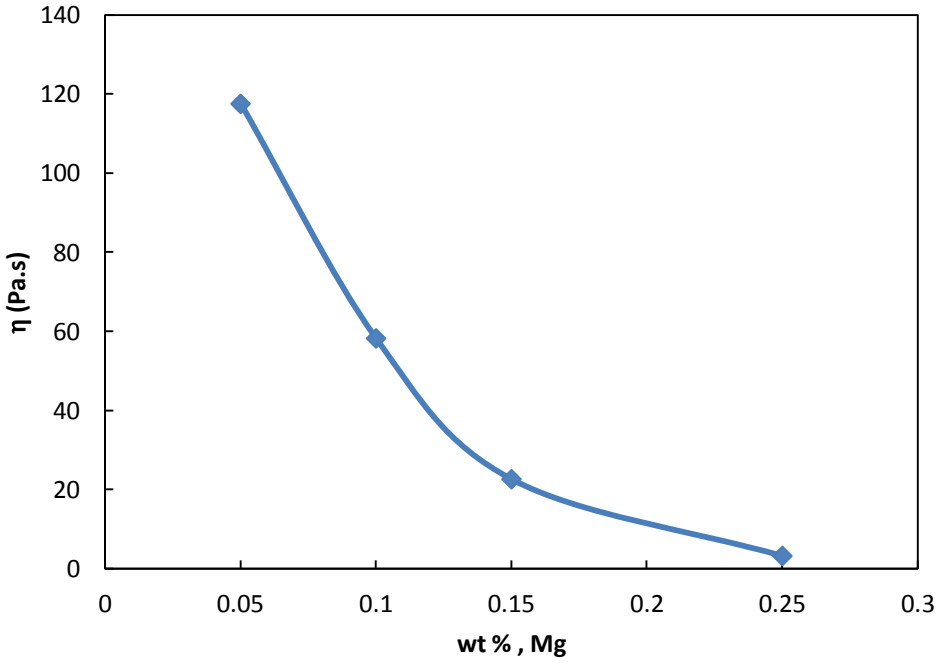

Figure 36: Effect of concentration of Magnesium ion on viscosity of PAM

From the Figure 36, it is observed that, η_o is decreasing as the ratio of weight of the PAM is decreasing from 0.95 % to 0.75 % PAM and simultaneously the ratio of magnesium ions concentrations is increasing in total solid concentration of 1 wt %. For the concentrations 0.05 %, 0.1 %, 0.15 % and 0.25 wt %, increase in magnesium ion, the zero

rate viscosities are 117.548, 58.22, 22.62, and 3.217 Pa.s, respectively. This is due to the concentration, molecules and network structure of the PAM. The resistance to flow offered by PAM decreases due to reaction of the magnesium cations with carboxylate anions of PAM as a result of decrease in the number of chains present in the PAM solution.

The effect of frequency sweep on the loss and storage modulus of the PAM in a magnesium ion solution as a function of concentration is observed from the Figures 37 and 38. As the frequency increases, it has been observed that both G″ and G′ gradually increase for a particular concentration. Also, it has been observed that with decrease in ratio of PAM weight and increase in magnesium ion concentration in the solution both the loss and storage modulus decreases. The storage modulus of weight ratio of (PAM/Mg) solutions with concentrations (0.95/0.05, 0.9/0.1, 0.85/0.15, 0.75/0.25), at an angular velocity of 0.0628 rad/s are 2.59, 1.31, 0.53 and 0.06 Pa, respectively.

From Figure 38, loss modulus of weight ratio of (PAM/Mg) solutions with concentrations (0.95/0.05, 0.9/0.1, 0.85/0.15, 0.75/0.25), at an angular velocity of 0.0628 rad/s are 2.42, 1.53, 0.8 and 0.18 Pa, respectively. For Concentrations of (PAM/Mg) with weight ratios (0.95/ 0.05 and 0.9/0.1), the G′ and G″ values are almost equal and that the slope of both these curves also is the same.

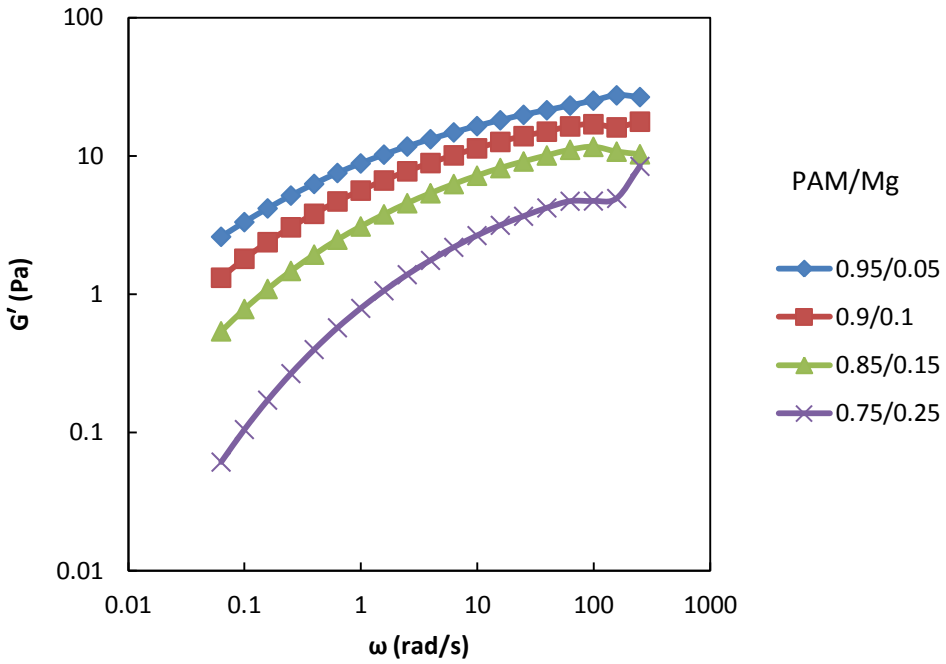

Figure 37: Effect of angular velocity on storage modulus of [PAM/Mg] solution

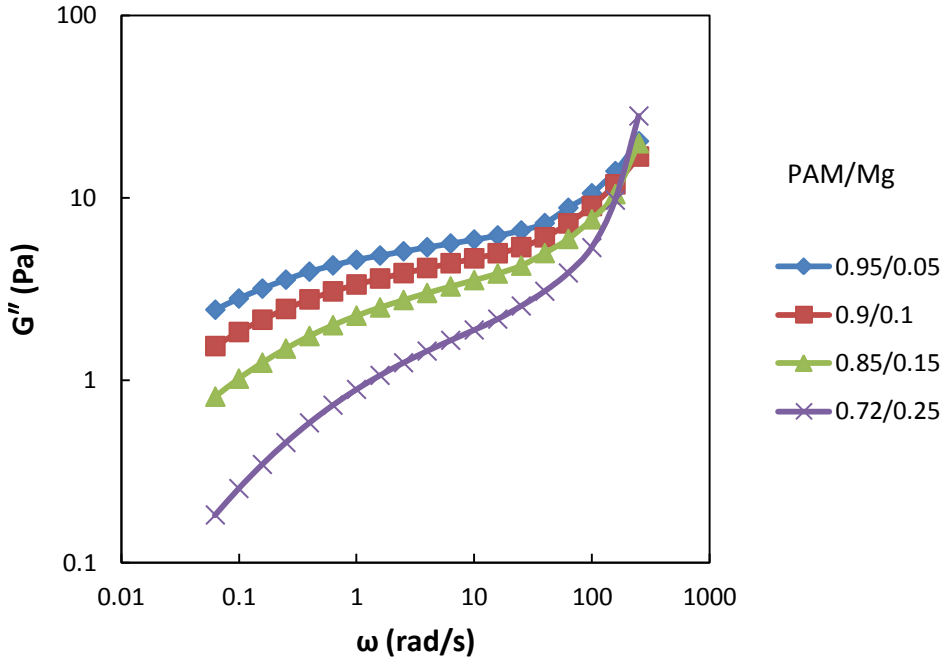

Figure 38: Effect of angular velocity on loss modulus of [PAM/Mg] solution

From both the Figures 37 and 38, the loss modulus G″ is less than storage elastic modulus G′ for weight ratios (0.95/0.05 and 0.9/0.1) of (PAM/Mg) solution, which means that for these solutions elastic component is stronger than the viscous component whereas for weight ratios (0.85/0.15 and 0.75/0.25) of (PAM/Mg) solution the storage elastic modulus G′ is less than loss modulus G″ hence for this solutions viscous component is stronger than elastic component.

In the Figures 39 and 40, the effect of angular velocity on the dynamic viscosity profile of the PAM in presence of magnesium ions is shown. The dynamic viscosity is decreasing with increase in angular frequency for all concentrations of (PAM/Mg) solutions with gram weight ratios (0.95/0.05, 0.9/0.1, 0.85/0.15, 0.75/0.25). The gel disintegrates at high shear rates and thus it can pass through porous media with less rupture to the chemical structure. PAM is a polyelectrolyte with negative charges on the carboxylate groups, hence there are strong interactions between polymer chains and magnesium ions (cations), causing repulsions between carboxylate anions to decrease thereby reducing the chains, and hence the viscosity is reduced.

For a mixture of (PAM/Mg) with weight ratio (0.95/0.05), as shown in Figure 39, the dynamic viscosity 38.58 Pa.s and out of phase component of viscosity in Figure 40 is 41.35 Pa.s at an angular velocity of 0.00628 rad/s and at 396 rad/s, the dynamic viscosity reduces to 0.06 Pa.s and out of phase component of viscosity is 0.07 Pa.s.

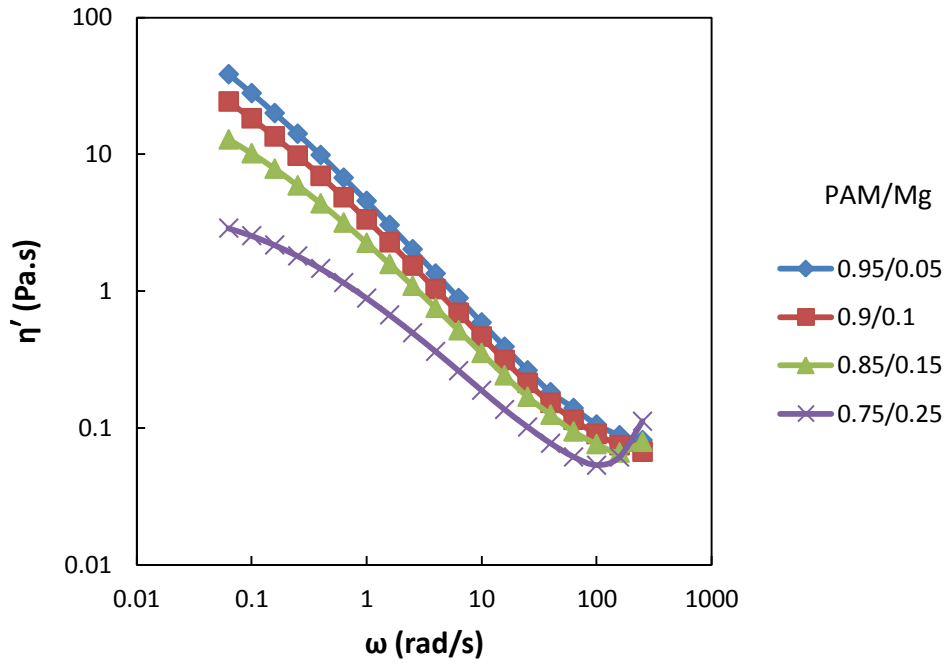

Figure 39: Effect of angular velocity on dynamic viscosity of [PAM/Mg] solution

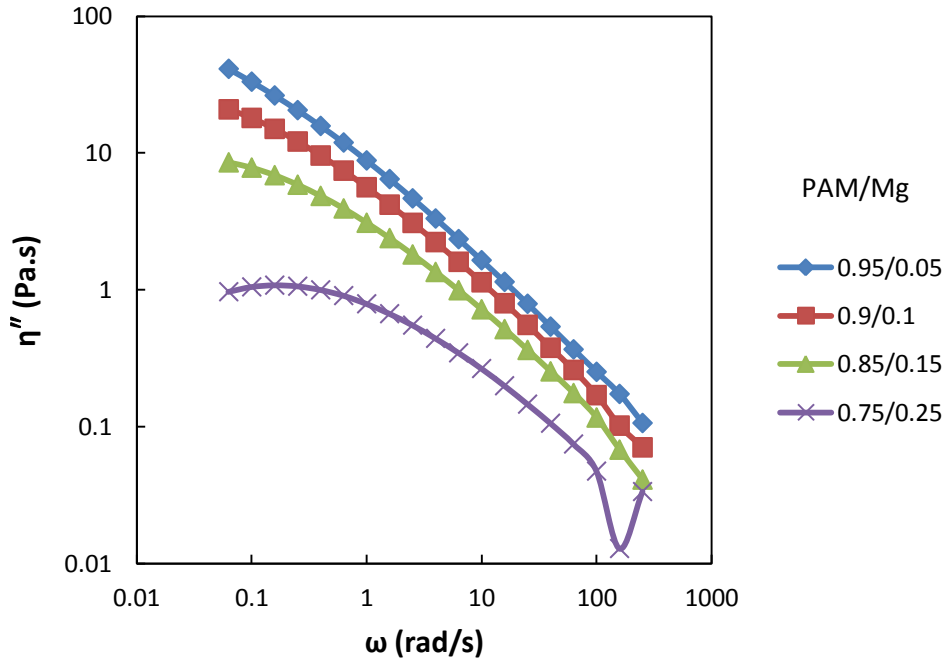

Figure 40: Effect of angular velocity on out of phase component of viscosity of [PAM/Mg] solution

At low angular velocity of 0.00628 rad/s, for solids content of 1 wt % in distilled water, as the ratio of PAM concentration was decreased and simultaneously ratio of magnesium ions was increased for weight ratios (0.9/0.1, 0.85/0.15 and 0.75/0.25) of (PAM/Mg) solution, the dynamic viscosities were reduced to 24.37, 12.87 and 2.89 Pa.s, respectively and the out of phase components of viscosities at same concentrations were 20.89, 8.56, and 0.97 Pa.s. Hence the addition of magnesium ions has a considerable impact on the dynamic viscosity and out of phase component of the PAM

At higher angular velocities of over 50 rad/s, it has been observed that for all the concentration the dynamic viscosities and out of phase component of viscosities are almost equal. All the values of dynamic viscosity and out of phase component of viscosity are approaching close to each other and become almost equal at high angular velocities of over 50 rad/s, this is due to the fact that at high frequency, the effect of frequency is more prominent as compared to effect of material properties like dynamic viscosity, out of phase component of viscosity etc. Hence the true response of material/PAM can only be observed at low frequency.

The Figure 41 and 42, show G' and G'' measured at room temperature $25^{o}C$ and subsequently increased to $70^{o}C$ to test its temperature withstanding ability. Both G' and G'' are almost straight lines for (PAM/Mg) solutions with weight ratios (0.95/0.05, 0.9/0.1 and 0.85/0.15)

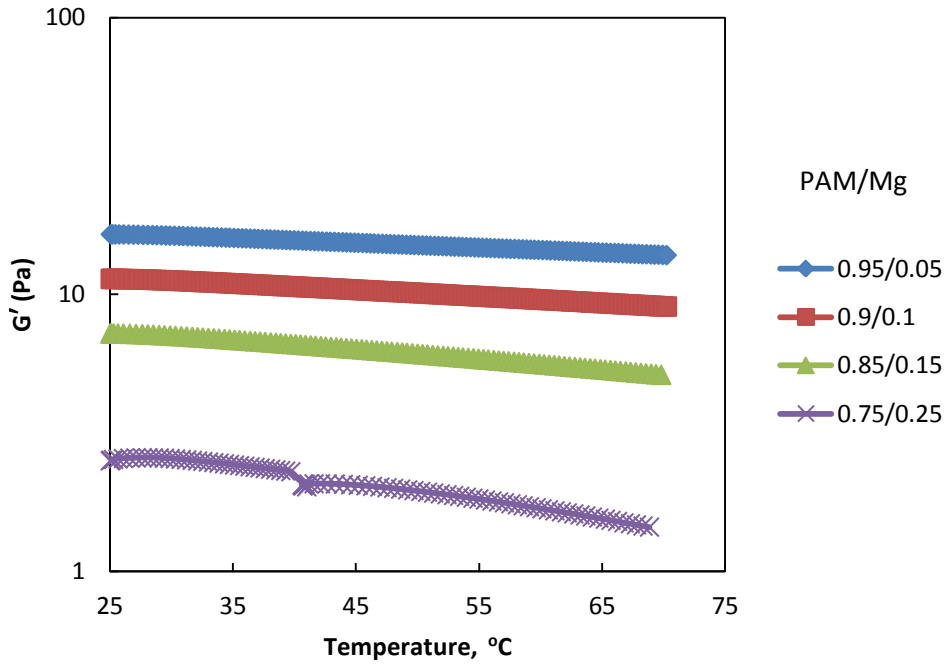

Figure 41: Effect of temperature on storage modulus of [PAM/Mg] solution

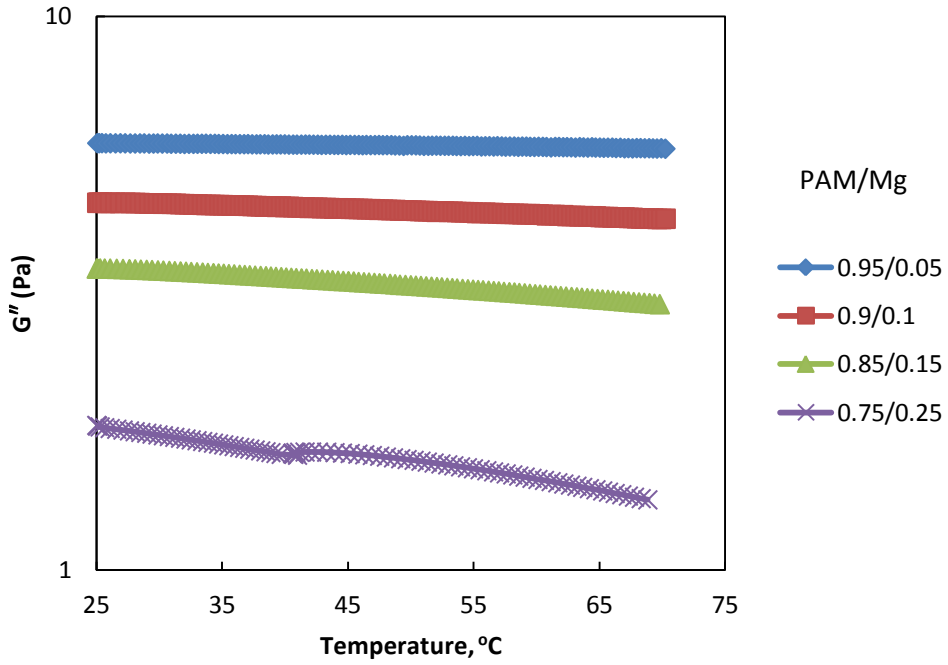

Figure 42: Effect of temperature on loss modulus of [PAM/Mg] solution

Therefore exposure to the temperature of 70°C is not affecting the properties of the PAM for small concentrations of 0.05, 0.1 and 0.15 wt % magnesium. But for the increase in the magnesium ion concentration to 0.25 wt % the stability of the PAM is falling from 70°C to around 40.6°C. Hence it can be concluded that as the concentrations of the magnesium is increased from 0.15 to 0.25 wt %, the thermal stability is decreases by 30°C for *Flopaam* sample 3330S.

4.3.3 Iron (Fe^{+3})

To study the effect of shear rate on the viscosity profile of the PAM in presence of Ferric ion, flow sweep test was conducted to obtain the relationship. The Figure 43 shows behavior of the viscosity with varying shear rate.

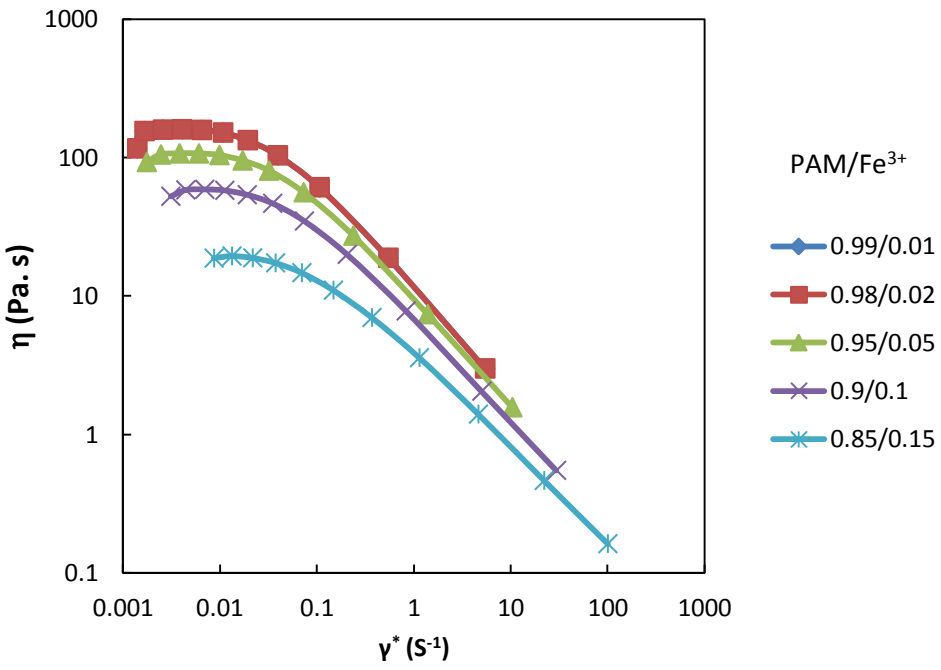

Figure 43: Effect of shear rate on viscosity of [PAM/Fe^{3+}] solution

The viscosity of the PAM in presence of ferric ion solution is decreasing with reduction in weight of the PAM from 0.95gm to 0.75gms and increase in weight of ferric ions from 0.05 to 0.25 g simultaneously. 0.95% weight of PAM in 0.05% wt of ferric, 0.9% weight of PAM in 0.1% wt of ferric and 0.85% weight of PAM in 0.15% wt of ferric have almost same viscosities at all the shear rates.

The viscosity of the PAM in presence of ferric ion was measured at zero shear rate, hence these viscosities measured are termed as zero rate viscosities. Carreau model was fit on the plot of η_o v/s γ to obtain zero rate viscosity for a particular concentration of PAM and ferric ion.

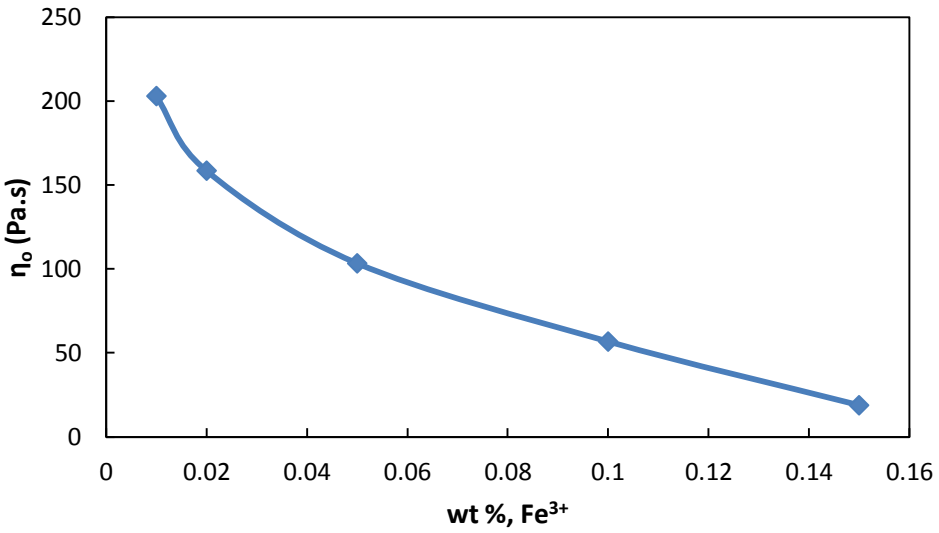

Figure 44: Effect of Ferric ion ratios on viscosity of PAM at zero shear rate

From the Figure 44, it is observed that, η_o is decreasing as the ratio of weight of the PAM is decreasing from 0.95 to 0.75 % PAM and simultaneously the ratio of ferric ions concentrations is increasing in total solids content of 1 wt %. For the concentrations 0.01, 0.02, 0.05, 0.1, and 0.15 wt %, increase in ferric ion, the zero rate viscosities are 203.07,

158.62, 103.44, 56.36, and 18.29 Pa.s, respectively. This is due to negative charges on the carboxylate groups of PAM, hence there are strong interactions between polymer chains and ferric ions (cations), causing repulsions between carboxylate anions to decrease thereby reducing the chains, and hence the viscosity is reduced.

The effect of frequency sweep on the loss and storage modulus of the PAM in a ferric ion solution as a function of concentration is observed from the Figure 45 and 46.

As the frequency increases, both G'' and G' gradually increase, with decrease in ratio of PAM weight and increase in ferric ion concentration in the solution both the loss and storage modulus decreases. The storage modulus of the (PAM/Fe) solutions with weight ratios (0.99/0.01, 0.98/0.02, 0.95/0.05, 0.9/0.1 and 0.85/0.15) at an angular velocity of 0.0628 rad/s are 3.5, 3.4, 2.41, 1.35 and 0.4 Pa, respectively.

From Figure 46, The loss modulus of the (PAM/Fe^{3+}) solutions with weight ratios (0.99/0.01, 0.98/0.02, 0.95/0.05, 0.9/0.1 and 0.85/0.15) at an angular velocity of 0.0628 rad/s are 3.3 Pa, 3.23 Pa, 2.55 Pa, 1.71 Pa and 0.76 Pa respectively. The (PAM/Fe^{3+}) solutions with weight ratios (0.99/0.01, 0.98/0.02 and 0.95/0.05) exhibit same behaviour. Hence it can be stated that very low concentration of iron in [PAM/Fe^{3+}] will not have much impact on the properties of PAM.

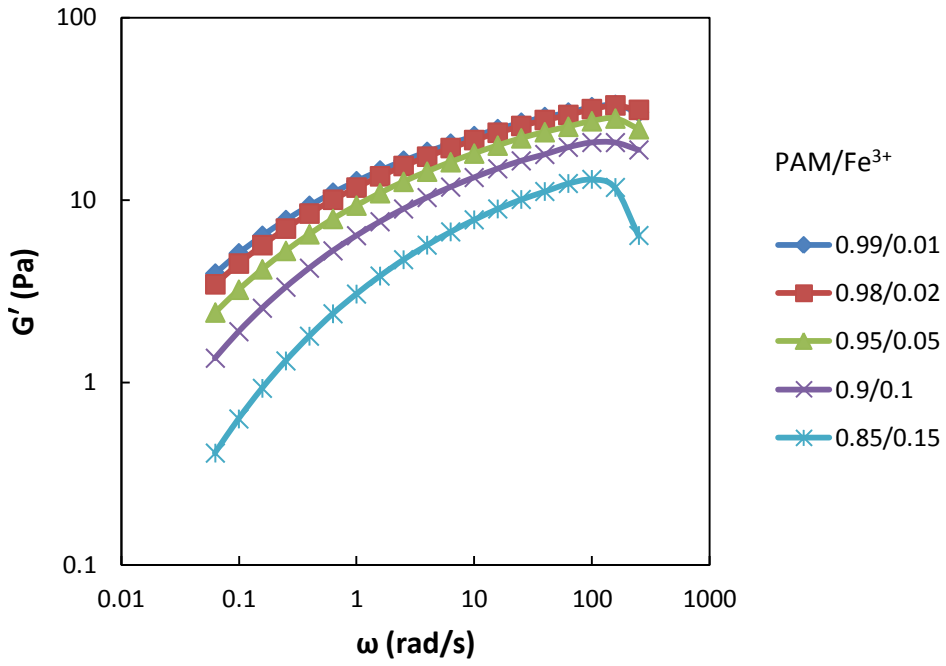

Figure 45: Effect of angular velocity on storage modulus of [PAM/Fe^{3+}] solution

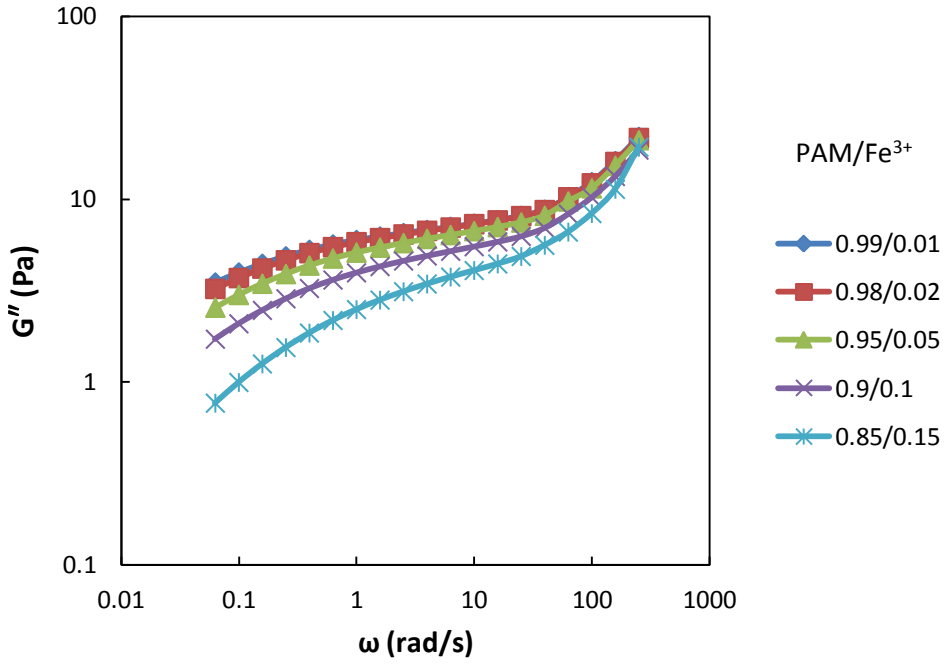

Figure 46: Effect of angular velocity on loss modulus of [PAM/Fe^{3+}]

From both the Figures 45 and 46, G′ of the (PAM/Fe^{3+}) solutions with weight ratios (0.99/0.01, 0.98/0.02 and 0.95/0.05) is higher than G″, hence for these solutions the elastic nature of the material dominates over viscous nature whereas for (PAM/Fe^{3+}) solutions with weight ratios (0.9/0.1 and 0.85/0.15) G″ is higher than G′, therefore viscous nature of the material dominates elastic nature.

At high angular velocities of over 50 rad/s it is observed that, storage modulus and loss modulus at all the concentrations of PAM in presence of ferric ion become almost equal. G′ and G″ at all concentrations become almost same at a very high frequency because at high angular velocities the effect of frequency is more prominent as compared to effect of material properties like temperature, concentration, modulus of elasticity, loss and storage modulus etc. Hence the true response of PAM behaviour can be observed at low frequency where the effect of materials is more prominent.

Figures 47 and 48 show the effect of angular velocity on the dynamic viscosity profile of the PAM in presence of ferric ion. The dynamic viscosity is decreasing with increase in angular frequency for all concentrations of the (PAM/Fe^{3+}) solutions with weight ratios (0.99/0.01, 0.98/0.02, 0.95/0.05, 0.9/0.1 and 0.85/0.15), upto 500 rad/s providing a shear thinning behaviour. Hence the gel disintegrates at high shear rates and thus it can pass through porous media with less rupture to the chemical structure. At an angular velocity of 0.00628 rad/s, (PAM/Fe^{3+}) solutions with weight ratios (0.99/0.01, 0.98/0.02 and 0.95/0.05) as shown in Figure 47, has a dynamic viscosity 51.47 Pa.s

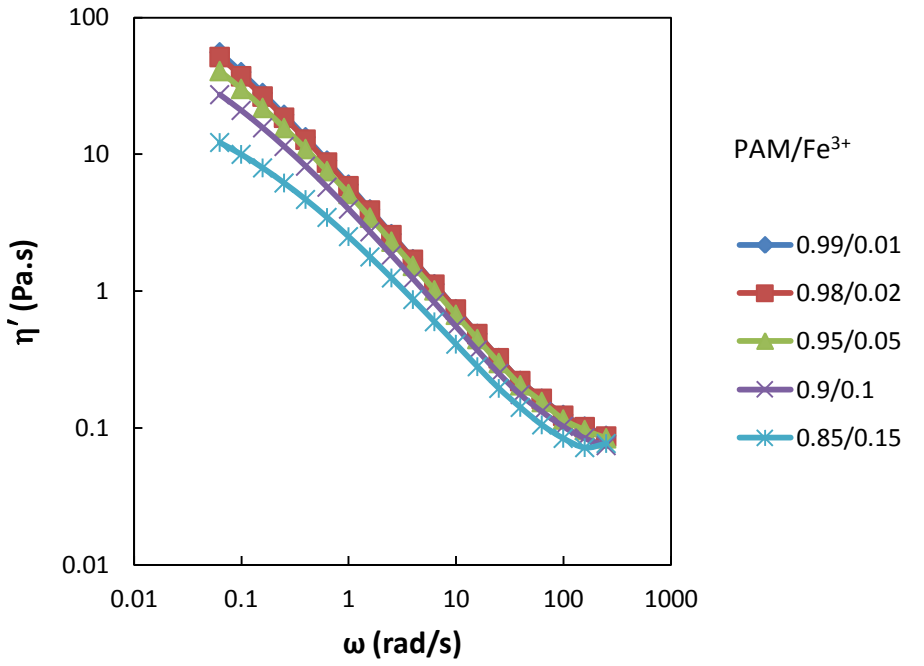

Figure 47: Effect of angular velocity on dynamic viscosity of [PAM/Fe^{3+}]

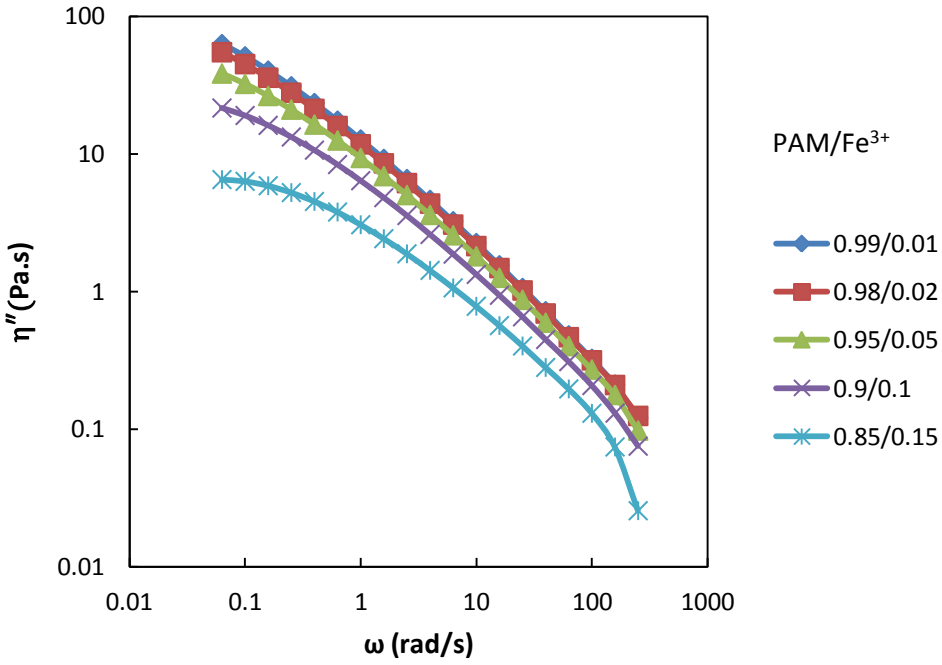

Figure 48: Effect of angular velocity on out of phase viscosity of [PAM/Fe^{3+}] solution

Out of phase component of viscosity as shown in Figure 48, is 38.41 Pa.s these viscosity values are decreasing to dynamic viscosity of 0.076 Pa.s and out of phase component of viscosity is 0.097 Pa.s, respectively with the increase in angular velocity to 396 rad/s.

At low angular velocity of 0.00628 rad/s, for a total solids content of 1 wt % in distilled water, as we decreased the ratio of PAM concentration in the solution and simultaneously increased the ferric ions wt % for a (PAM/Fe^{3+}) solutions with weight ratios (0.9/0.1 and 0.85/0.15) the dynamic viscosities were reduced to 27.3 and 12.3 Pa.s, respectively and the out of phase components of viscosities at same concentrations were 21.56 and 6.51 Pa.s. Hence the addition of ferric ions has a considerable impact in decreasing the dynamic viscosities and out of phase component of viscosities of PAM.

The Figures 49 and 50, show G' and G'' measured at room temperature 25^oC and subsequently the temperature was increased upto 70^oC inorder to test its temperature withstanding ability. The temperature was increased in short intervals upto 70^oC. Both G' and G'' are almost straight lines for all solutions with (PAM/Fe^{3+}) concentrations consisting weight ratios (0.99/0.01, 0.98/0.02, 0.95/0.05, 0.9/0.1 and 0.85/0.15). There is hardly any deviation of the points from the straight line at all the temperatures for these two mixtures upto 70^oC. The graph suggests that exposure to the temperature of 70^oC is not affecting the properties of the polyacrylamide for all concentrations of 0.01, 0.02, 0.05, 0.1 and 0.15 wt %.

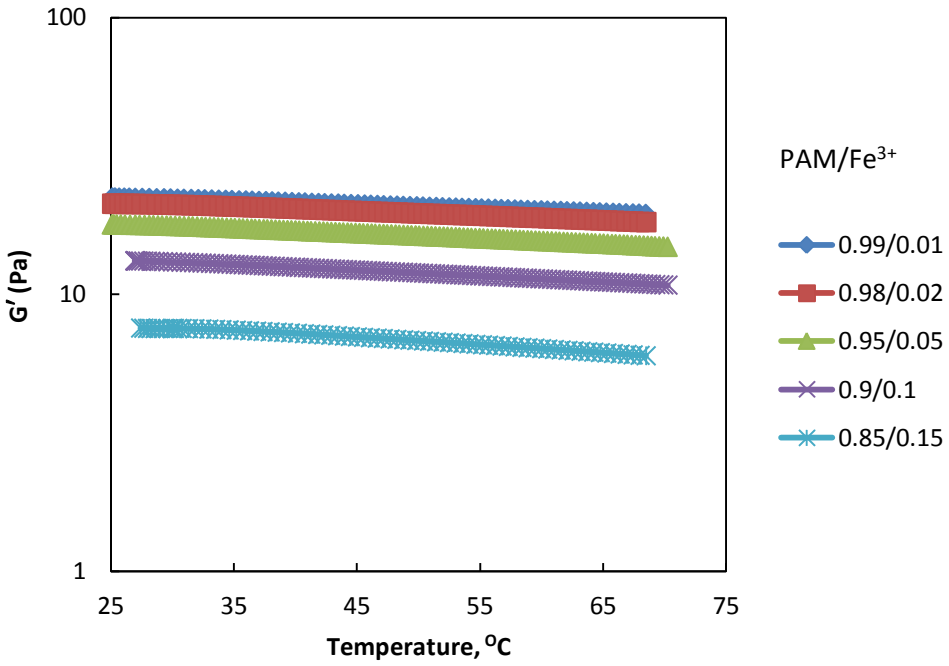

Figure 49: Effect of temperature on storage modulus of [PAM/Fe^{3+}]

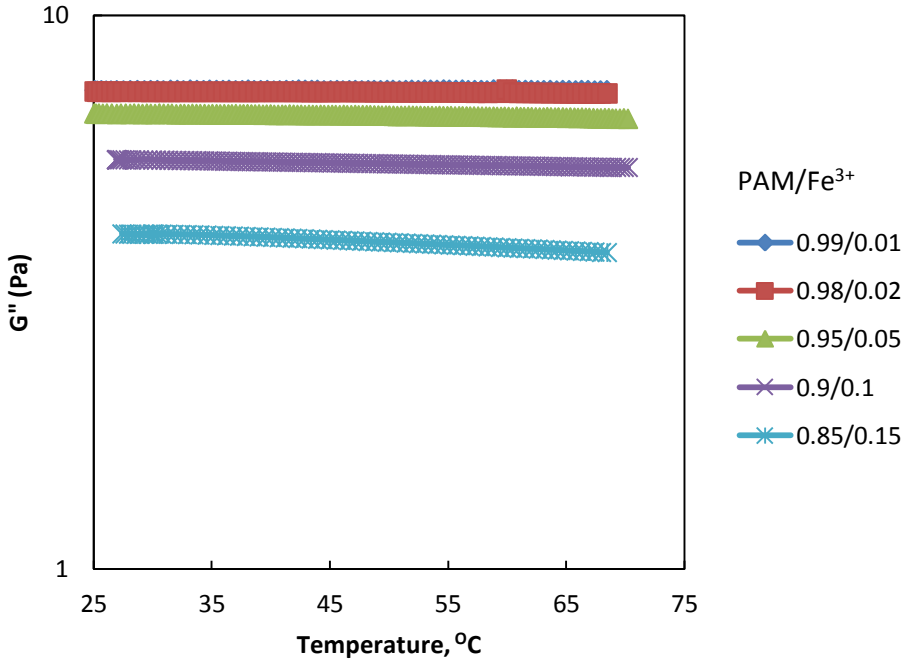

Figure 50: Effect of temperature on loss modulus of [PAM/Fe^{3+}]

Ferric ions since the loss and storage modulus remain same at a temperature range of 25-70^{o}C. Hence all the concentrations of PAM which are soluble in distilled water in presence of iron don't have any impact on the thermal stability of the pure PAM.

4.3.4 Manganese (Mn^{+2})

To study the effect of shear rate on the viscosity profile of the PAM in presence of Manganese ion, flow sweep test was conducted to obtain the relationship. The Figure 51 shows behavior of the viscosity with varying shear rate.

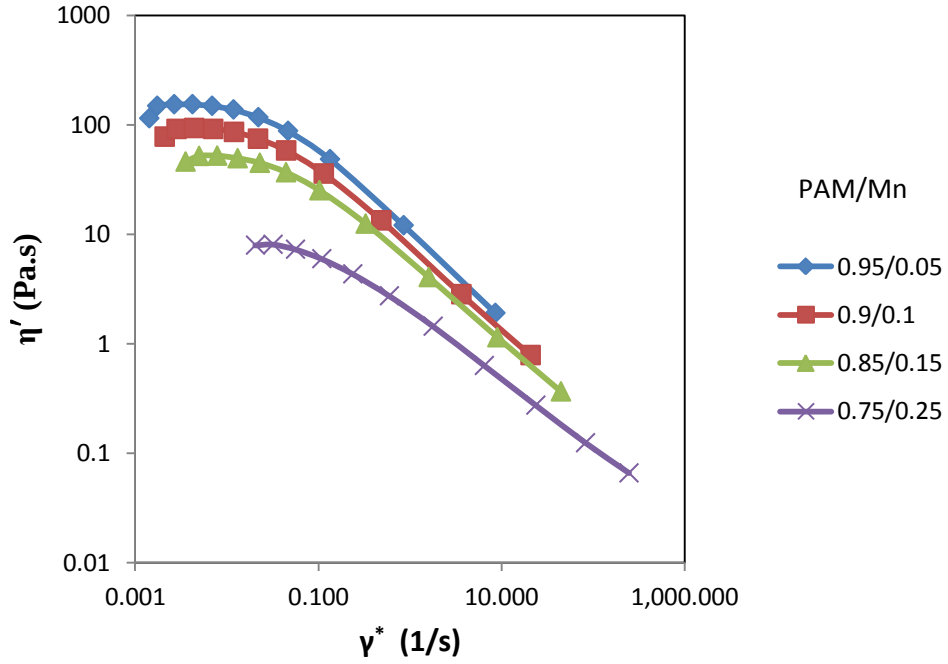

Figure 51: Effect of Shear rate on viscosity of [PAM/Mn]

The viscosity of the Polyacrylamide in presence of manganese ion solution is decreasing with reduction in weight of the PAM from 0.95 to 0.75 % and increase in weight of manganese ions from 0.05 g to 0.25 g simultaneously. (PAM/Mn) solution with weight

ratios (0.95/0.05 and 0.9/0.1) have almost same viscosities at all the shear rates. Hence the concentration which is cost effective can be prepared as both the properties will remain same.

The viscosity of the PAM in presence of manganese ion was measured at zero shear rate, hence these viscosities measured are termed as zero rate viscosities. Carreau model was fit on the plot of η_o v/s $\dot{\gamma}$ to obtain zero rate viscosity for a particular concentration of PAM and manganese ion. These η_o were plotted against concentration of the manganese to study its impact.

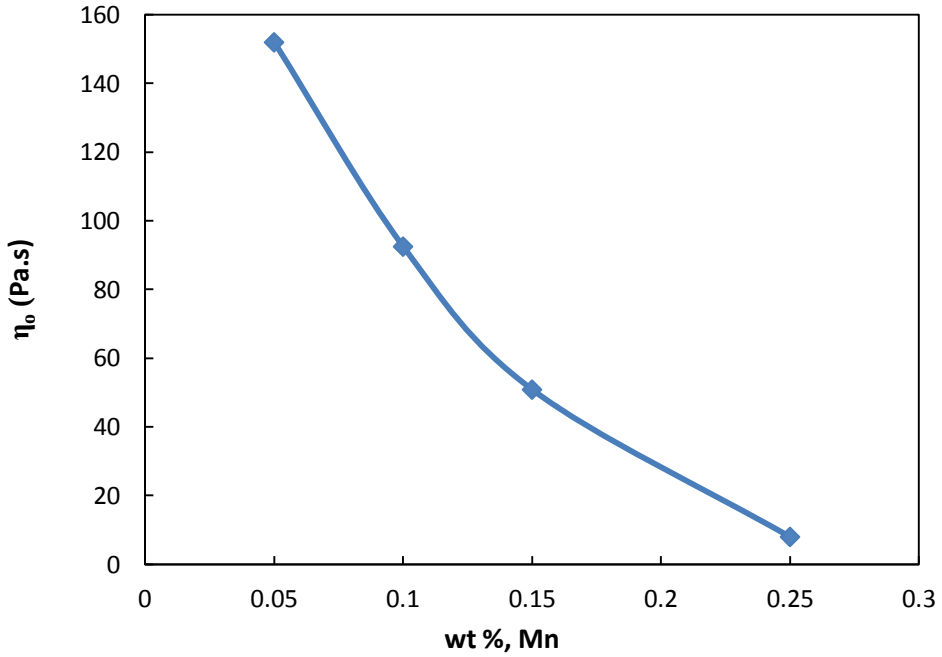

Figure 52: Effect of concentration of manganese ion on viscosity of PAM at zero shear rate

From the Figure 52, it is observed that, η_o is decreasing as the ratio of weight of the PAM is decreasing from 0.95 g to 0.75 g PAM and simultaneously the ratio of manganese ions concentrations is increasing in total solids 1wt % solution. For the concentrations 0.05,

0.1, 0.15 and 0.25 wt % increase, in manganese ion, the zero rate viscosities are 151.95, 92.49, 50.87, and 8 Pa.s, respectively. This is due to concentration, molecules and network structure of the partially hydrolyzed PAM. It is a polyelectrolyte with negative charges on the carboxylate groups, hence there are strong interactions between polymer chains and manganese ions (cations), causing repulsions between carboxylate anions to decrease thereby reducing the chains, and hence the viscosity is reduced.

The effect of frequency sweep on the loss and storage modulus of the PAM in a Manganese ion solution as a function of concentration is observed from the Figure 53. As the frequency increases, it has been observed that both G″ and G′ gradually increase for a particular concentration and with decrease in ratio of PAM weight and increase in manganese ion concentration in the solution both the loss and storage modulus decreases. The storage modulus of the (PAM/Mn) solutions with weight ratios (0.95/0.05, 0.9/0.1, 0.85/0.15 and 0.75/0.25) at an angular velocity of 0.0628 rad/s are 3.295, 1.98 Pa, 1.18 Pa and 0.18 Pa, respectively.

From Figure 54, loss modulus of the (PAM/Mn) solutions with weight ratios (0.95/0.05, 0.9/0.1, 0.85/0.15 and 0.75/0.25) at an angular velocity of 0.0628 rad/s are 3.01, 2.05, 1.427 and 0.36 Pa, respectively. Also it has been observed that for (PAM/Mn) solution with weight ratio (0.95/0.05) and (0.9/0.1), the G″ values are almost equal and that the slope of both these curves also is the same.

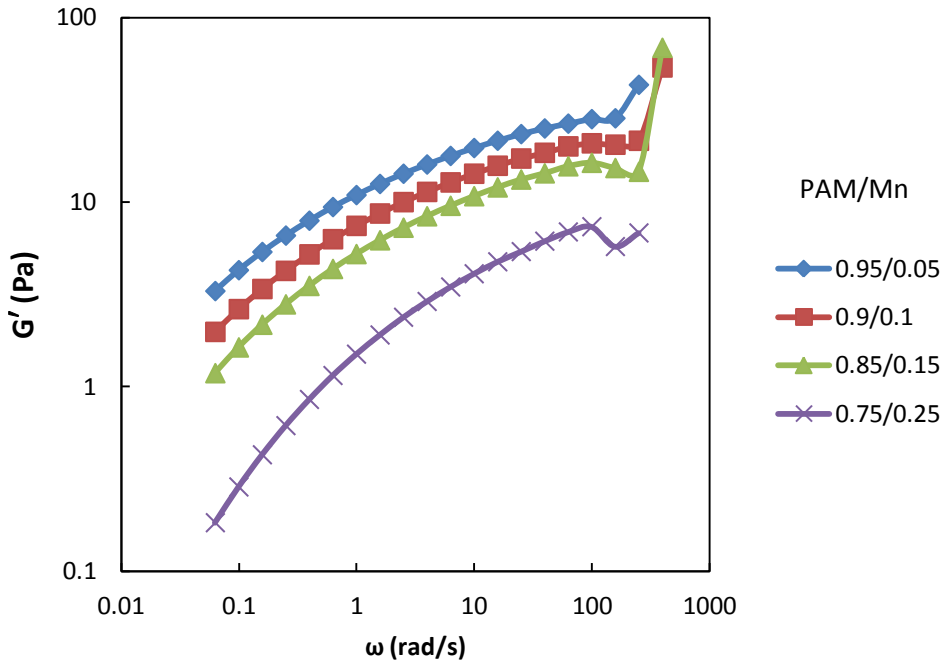

Figure 53: Effect of angular velocity on storage modulus of [PAM/Mn] solution

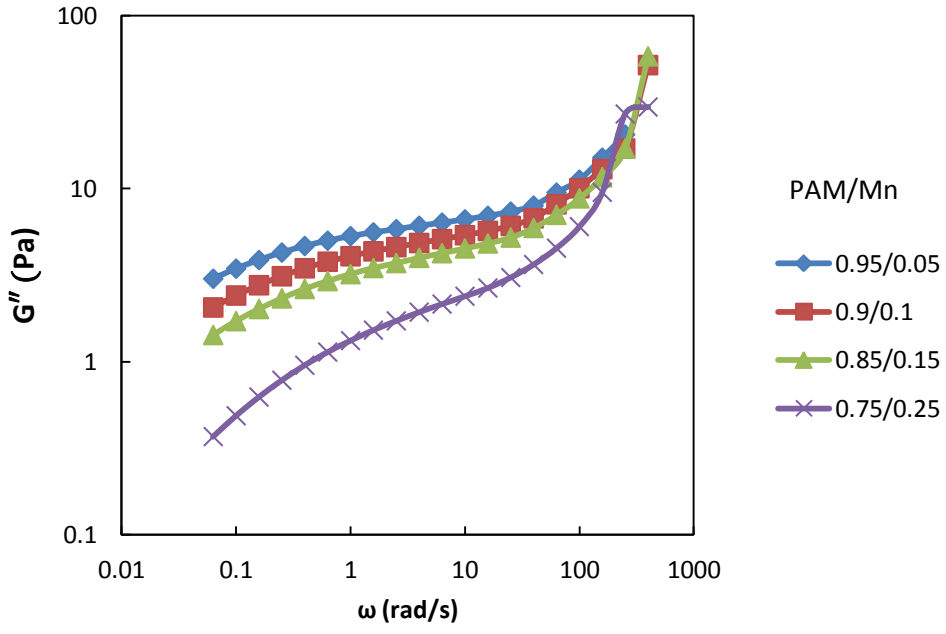

Figure 54: Effect of angular velocity on loss modulus of [PAM/Mn] solution

From both the Figures 53 and 54, the loss modulus G″ is greater than G′ for (PAM/Mn) solution with weight ratio (0.75/0.25), hence for this concentration the viscous component is more predominant over the elastic component whereas for (PAM/Mn) solutions with weight ratios (0.95/0.05, 0.9/0.1 and 0.85/0.15) it is vice versa.

In the Figures 55 and 56, the effect of angular velocity on the dynamic viscosity profile of the PAM in presence of manganese ions is shown. The dynamic viscosity is decreasing with increase in angular frequency for all (PAM/Mn) solutions. The reduction of dynamic viscosity can be attributed to the interactions between anions of polymer chains and positive manganese ions. For mixtures (PAM/Mn) solutions with weight ratios (0.95/0.05, 0.9/0.1, 0.85/0.15 and 0.75/0.25), the dynamic viscosities are 48.02, 32.71, 22.72 and 5.87 Pa.s, respectively.

This shows that as the ratio of manganese increased, there is a decrease in the dynamic viscosity. Similarly the out of phase component of viscosities are 52.49, 31.52, 18.5 and 2.91 Pa.s, respectively as shown in Figure 56, at an angular velocity of 0.00628 rad/s and are decreasing with increase in angular frequency.

This is due to concentration, molecules and network structure of the partially hydrolyzed PAM. It is a polyelectrolyte with negative charges on the carboxylate groups, hence there are strong interactions between polymer chains and manganese ions (cations), causing repulsions between carboxylate anions to decrease thereby reducing the chains, and hence the viscosity is reduced.

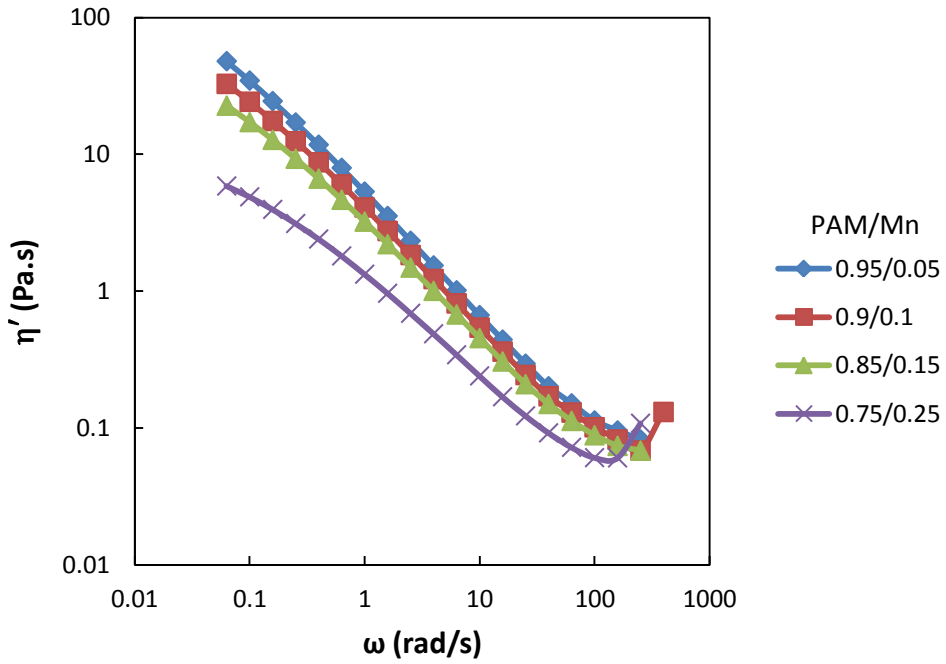

Figure 55: Effect of angular velocity on dynamic viscosity of [PAM/Mn]

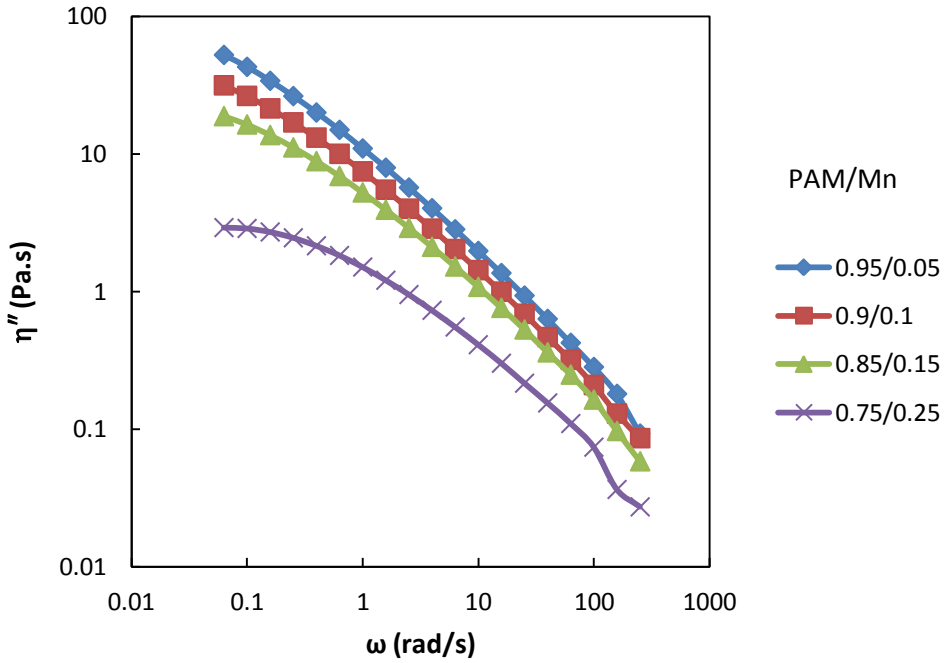

Figure 56: Effect of angular velocity on out of phase component of viscosity of [PAM/Mn] solution

For lost circulation agents, thermal stability is a very important criteria as in downhole the seal formed by the lost circulation materials has to withstand very high temperatures of formations. Sample used was *Flopaam 3330s* and the thermal stability according to the manufacturer is around 70^{o}C. Hence, the PAM needs to be tested for its stability at various concentrations to check if concentration is having any impact on thermal stability. In the earlier cases (Figure 24 and 25) the pure PAM solution was thermally stable at all the concentrations. Now the effect of counterions on the thermal stability of the PAM is being tested.

The Figures 57 and 58, show G′ and G″ measured at room temperature 25^{0}C and subsequently temperature was increased in intervals upto 70^{0}C. Both G′ and G″ are deviating at 39^{0}C for (PAM/Mn) solutions for weight ratios (0.75/0.25). Hence we can conclude that as the percentage of manganese is increased from 15 to 25 wt %, the stability of the [PAM/Mn] is affected and it is reduced by around 31^{0}C. For (PAM/Mn) solution with weight ratio (0.75/0.15), the thermal stability of the solution fails around 39^{o}C. Hence it can be concluded that by addition of manganese beyond 0.15 g to the total solids weight of 1 g the thermal stability fails is reduced by 30^{o}C.

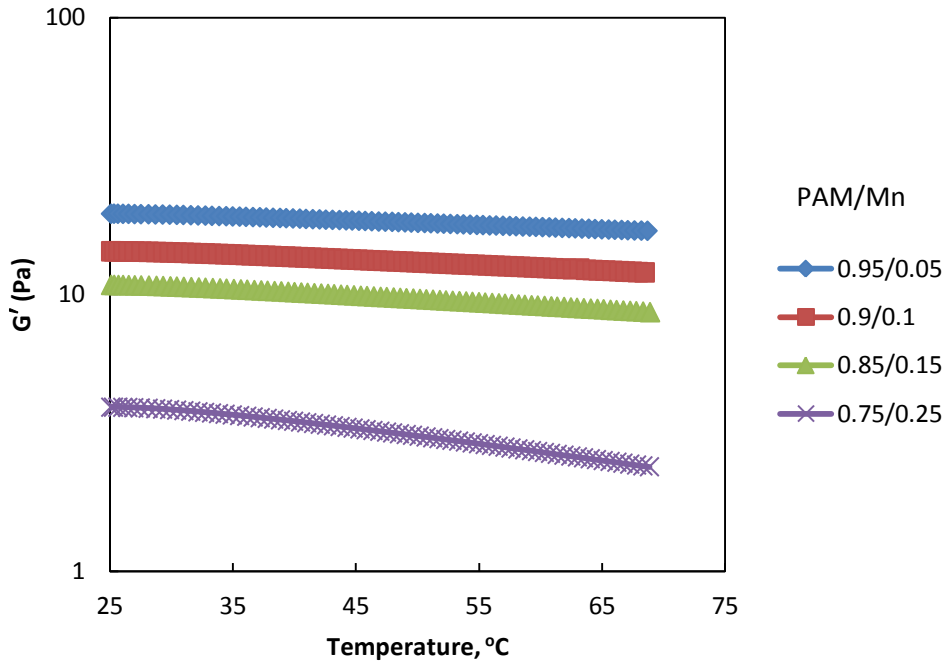

Figure 57: Effect of Temperature on storage modulus of [PAM/Mn]

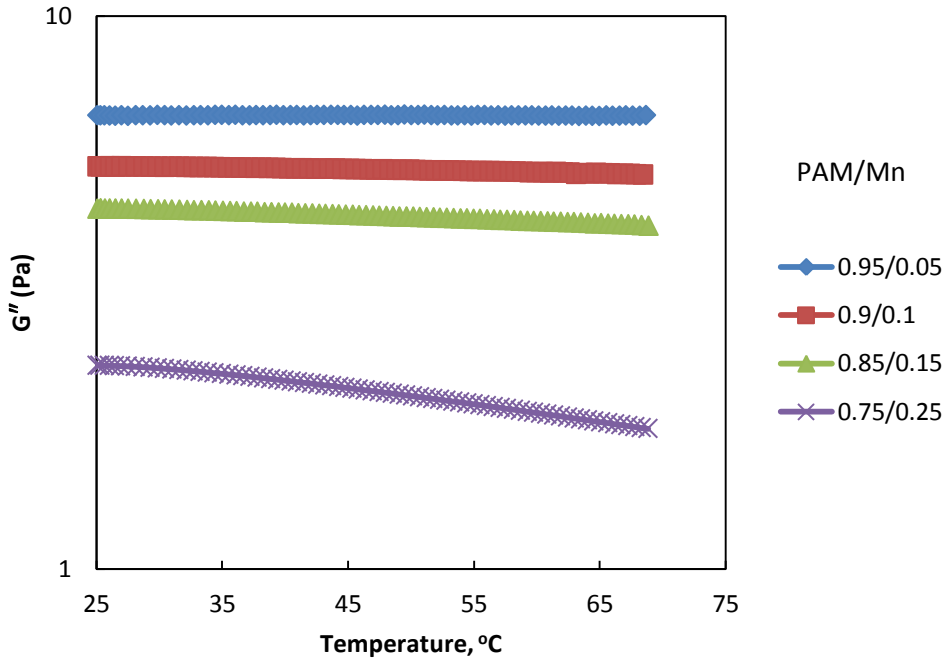

Figure 58: Effect of Temperature on loss modulus of [PAM/Mn] solution

4.4 Crosslinking of PAM/PEI to form gelation in presence of manganese

It is believed that the gelation takes place between PAM/PEI due to transamidation mechanism [19] as shown in Figure 59. This reaction is a substitution reaction where nucleophilic amine nitrogen on PEI replaces the amide groups on the polymer chains. Al-Muntasheri et al. (2008) concluded that the PEI/PAM can be crosslinked at temperatures upto 140 C and pressure of 30 bars [52].

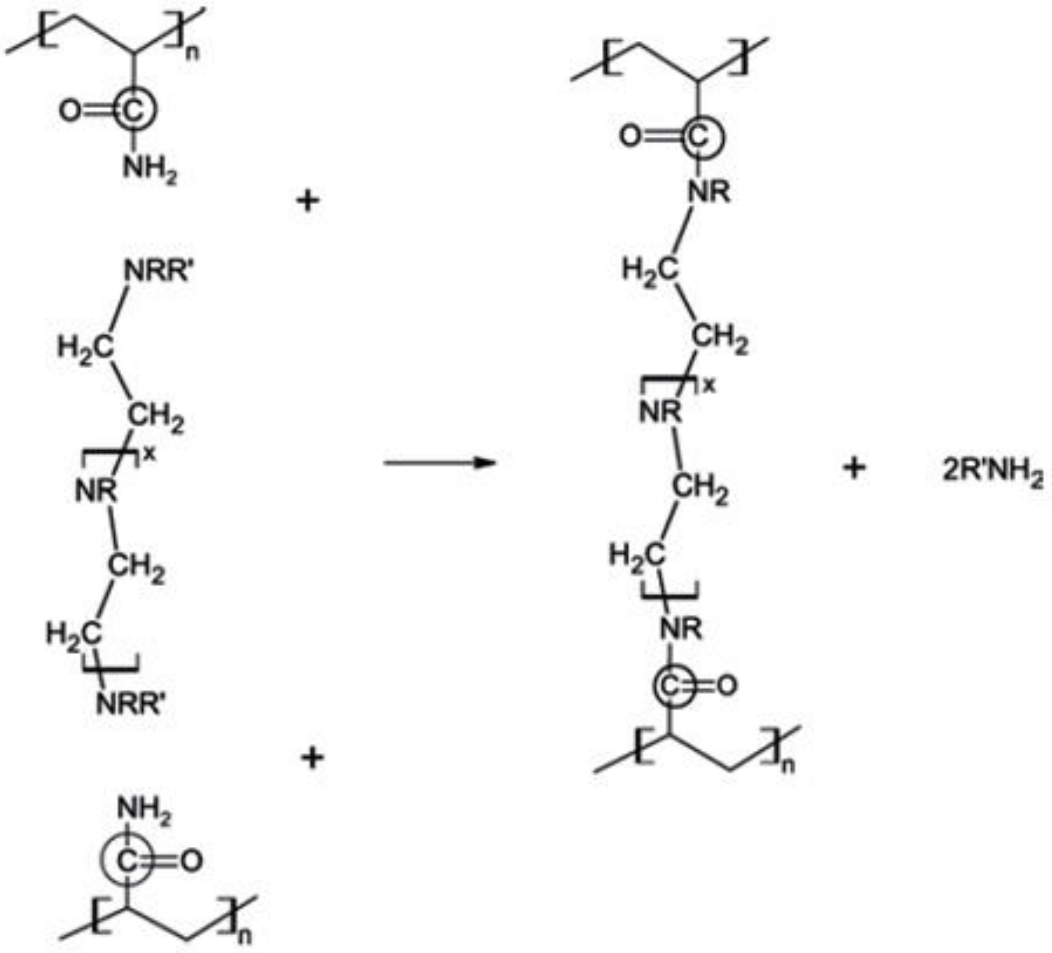

Figure 59: PAM/PEI gelation reaction [44]

One of the major finding of this research thesis is the use of small percentage of metal ions to make elastic component of the fluid stronger than viscous, also among the various metal ions used, it was observed that manganese results in very little viscosity drop. Manganese is being used for the first time in the preparation of LCM, in this research work to make the gel formed behave elastic than viscous i.e. to make storage modulus (G′) is stronger than loss modulus (G″), so that the gel behave more solid like elastic to take the shape of the fractures and seal them without damaging the formation. Figure 60 shows the reaction of PAM/PEI in presence of manganese ions.

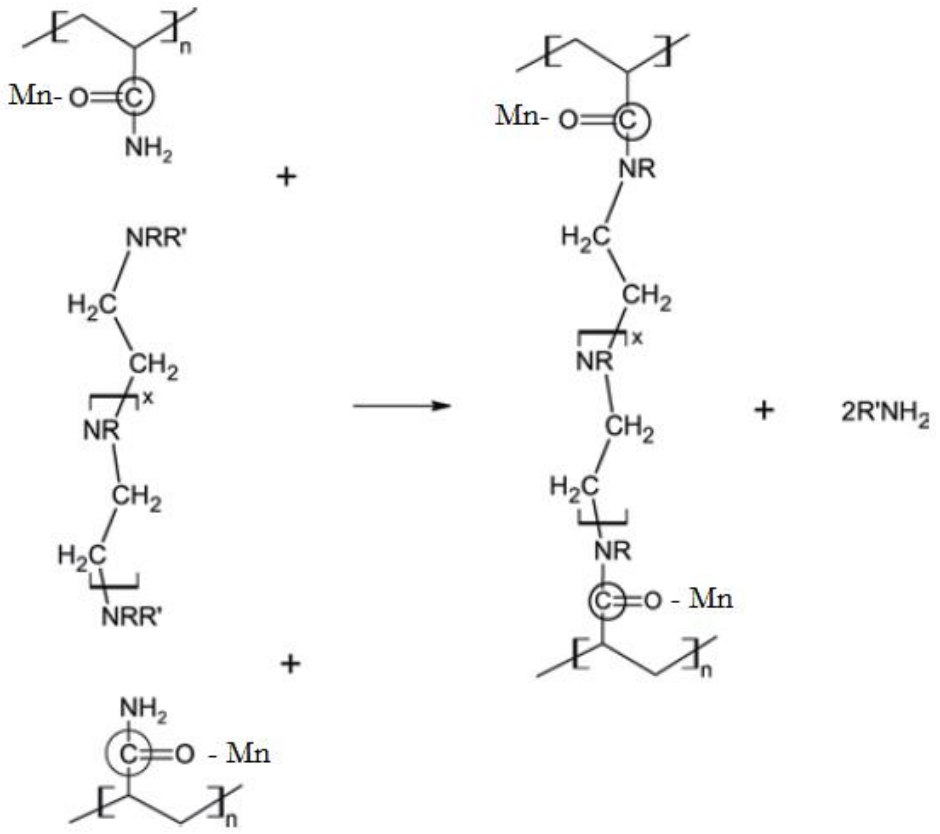

Figure 60: PAM/PEI gelation in presence of manganese ion

From the Figure 61, the viscosity of the PAM/PEI in presence of manganese ion solution is decreasing with increase in shear rate, exhibiting a shear thinning behaviour. From a viscosity of 763.8 Pa.s at a shear rate of $0.001s^{-1}$, decreased to 81.133 Pa.s at 0.12 s^{-1} shear rate.

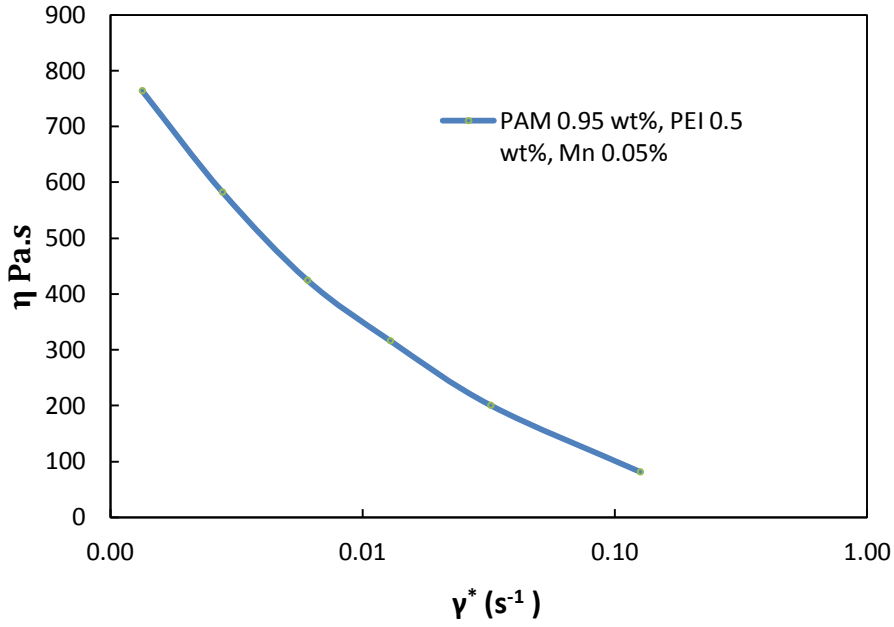

Figure 61: Effect of shear rate on viscosity of [PAM/PEI/Mn] solution

The effect of frequency sweep on the loss and storage modulus of the PAM/PEI in presence of manganese ions as a function of concentration is observed from the Figure 62. As the frequency increases, both G″ and G′ gradually increase for a particular concentration and with decrease in ratio of PAM weight and increase in manganese ion concentration in the solution both the loss and storage modulus decreases. From the figure it is observed that G' value is around 10 times greater than G" value indicating that the elastic nature of gel dominates over its viscous nature. In the Figure 63, the effect of angular velocity on the dynamic viscosity profile of the PAM/PEI in presence of manganese ions is studied. The dynamic viscosity is decreasing with increase in angular

frequency for a (PAM/PEI/Mn) solution with weight ratio (0.95/0.5/0.05), upto 500 rad/s providing a shear thinning behaviour. Hence the gel disintegrates at high shear rates and thus it can pass through porous media with less rupture to the chemical structure.

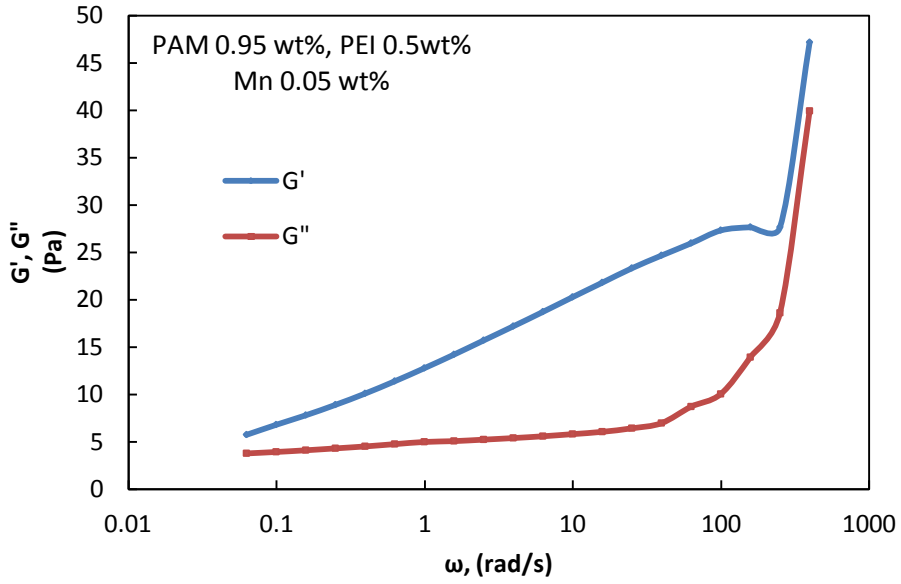

Figure 62: Effect of angular velocity on storage and loss modulus of [PAM/PEI/Mn] solution

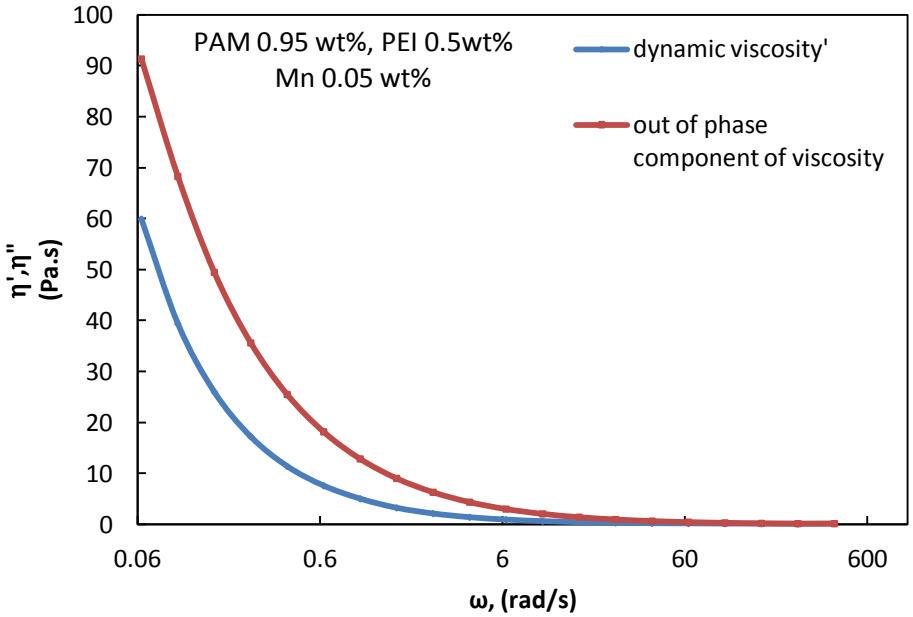

Figure 63: Effect of angular velocity on storage and loss modulus of [PAM/PEI/Mn] solution

4.5 Comparison of effects of rheology of counterions/crosslinker on viscosity profile of PAM

Figure 64, shows the effect of 0.05 wt % concentration of various counterions in presence of 0.95 wt % concentration on viscosity of PAM at zero shear rate. The viscosity of pure 1wt % concentration of PAM is 170.4 Pa. s. For a 0.95% concentration of PAM mixed with a concentration of 0.05 wt % of counterions manganese, magnesium, iron and calcium, the zero rate viscosities become 152, 117.5, 103.4 and 90.3 Pa.s, respectively. The calcium ion has a huge impact in decreasing the viscosity of the PAM as it decreases the viscosity by almost 47% whereas the manganese doesn't seem to have much impact on the PAM viscosity, with the decrease in percentage is around 10% only.

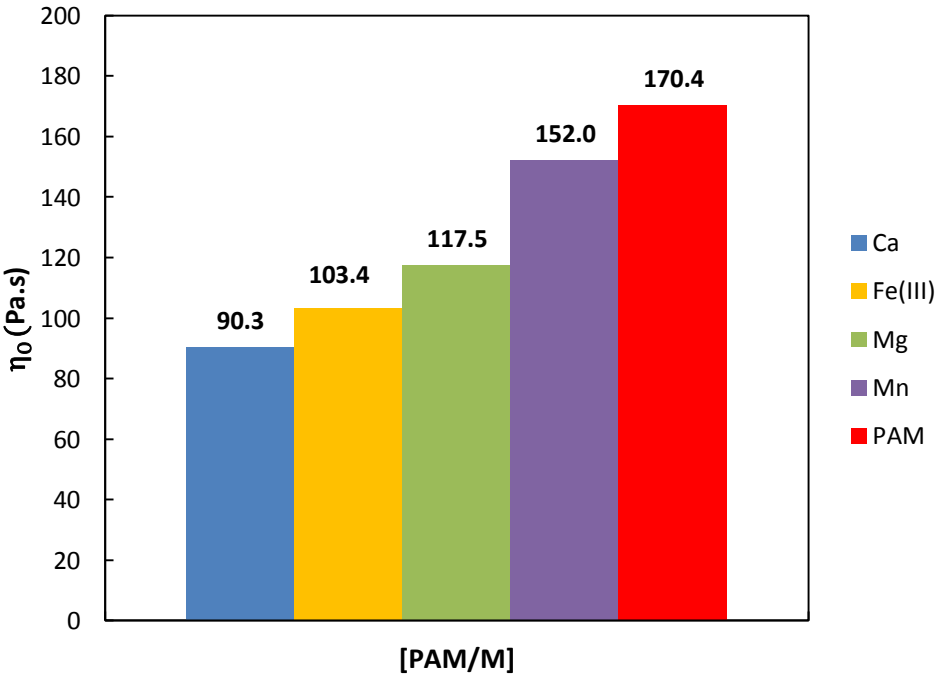

Figure 64: Comparison of viscosity of PAM with [PAM/M = 0.95/0.05] solution

Figure 65 shows the comparison of zero rate viscosities of pure PAM solution and (PAM/Metal ions) solution with weight ratio (0.9/0.1).The viscosity of Pure 1 wt % concentration of PAM is 170.4 Pa. s. For the (PAM/M) solutions with weight ratio (0.9/0.1) the zero rate viscosities were 92.5, 58.2, 56.9 and 31.3 Pa.s, for manganese, magnesium, iron and calcium respectively.

Recovery of viscosity by manganese is appreciable when compared to other ions and calcium is causing a considerable decrease in the viscosity of PAM. These effects of the PAM should be incorporated while designing the LCM as viscosity plays an important factor for sealing the zones

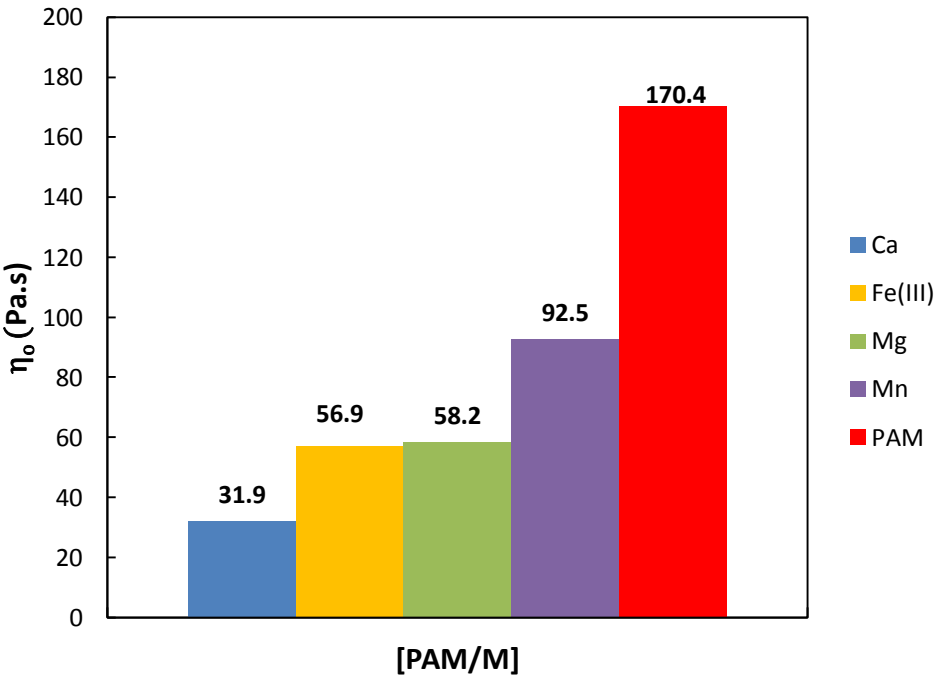

Figure 65: Comparison of viscosity of PAM with [PAM/M = 0.9/0.1] solution

Figure 66 shows the comparison of zero rate viscosities of pure PAM solution and (PAM/Metal ions) solution with weight ratio (0.9/0.1).The viscosity of Pure 1 wt % concentration of PAM is 170.4 Pa. s. For the (PAM/M) solutions with weight ratio (0.9/0.1) the zero rate viscosities for manganese, magnesium, iron and calcium are 50.9, 22.6, 18.9 and 4.3 Pa.s respectively.

Hence is can be concluded that, when 0.15 wt % of calcium added to a solution containing 0.85 wt % PAM, the overall viscosity of the system deteriorates and care must be taken while introducing calcium along with lost circulation material containing PAM. These effects will help in the designing of the LCM.

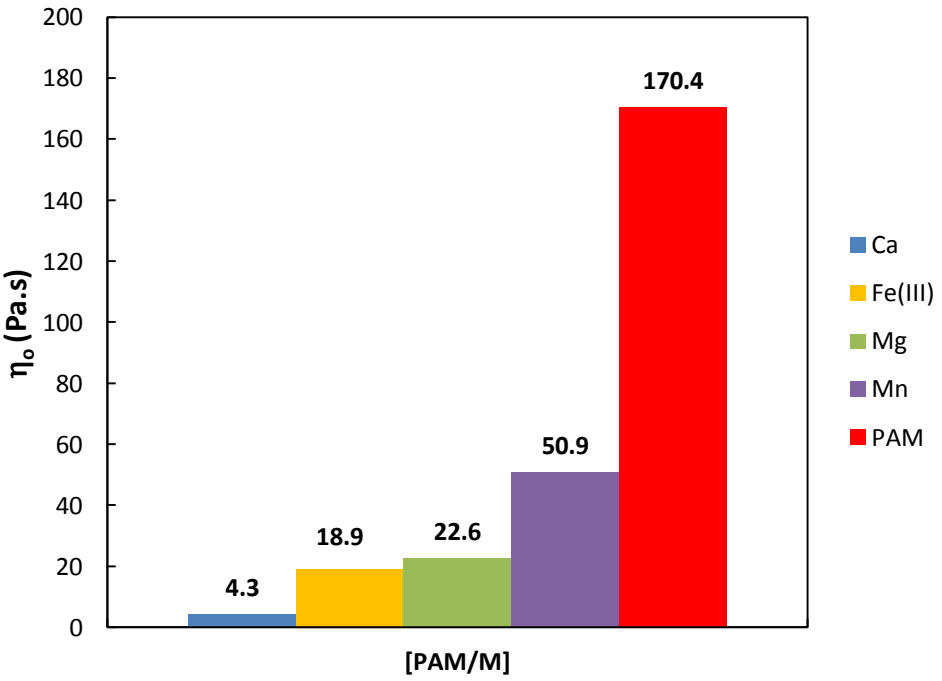

Figure 66: Comparison of viscosity of PAM with [PAM/M = 0.85/0.15] solution

Figure 67 shows the effect of 0.25 wt % concentration of various counterions in presence of 0.75 wt % concentration on Viscosity of PAM at zero shear rate. The viscosity of pure 1% wt concentration of PAM is 170.4 Pa. s when a 0.75% concentration of PAM mixed with a concentration of 0.25% of counterions manganese, magnesium and calcium, the zero rate viscosities become 8.1, 3.22, and 0.7 Pa.s, respectively.

Iron comparison is not included in Figure 67 as it doesn't dissolve at this concentration and the flakes or precipitate is formed in PAM solution and therefore it is not suitable for carrying out the experiment. The calcium ion has a huge impact in decreasing the viscosity of the PAM with 99.58% reduction and in this case the manganese decreases the viscosity by 95.3%.

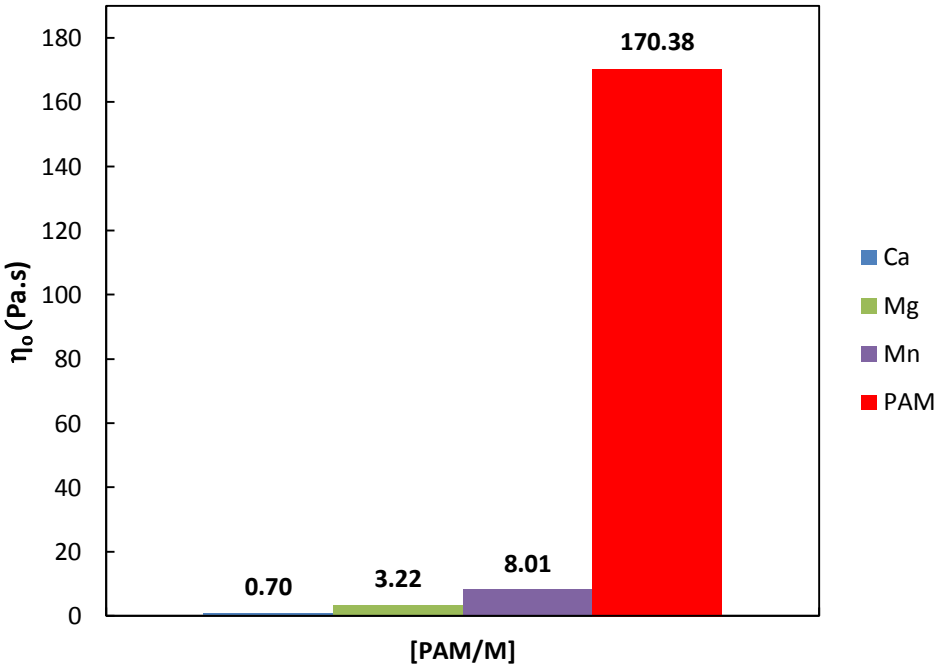

Figure 67: Comparison of viscosity of PAM with [PAM/M = 0.75/0.25] solution

Figure 68, shows comparison of viscosity at zero shear rate between solutions of [PAM/Mn] with weight ratio [0.95/0.05], pure 1 wt% PAM solution, and a solution with PAM 0.95 wt%, Mn 0.05 wt% and PEI 0.5 wt%. The viscosity of [PAM/Mn] with weight ratio [0.95/0.05] and pure 1wt % concentration of PAM are 151.95 and 170.4 Pa. s respectively but for a solution 0.95% concentration of PAM mixed 0.05 wt % of counterions manganese and 0.5 wt% organic crosslinker PEI there is huge increase in viscosity by 5 - 7 times and the viscosity of the resulting solution becomes 1105 Pa.s. This high increase in the viscosity is due to the gelation that takes place between PAM/PEI due to transamidation mechanisms.

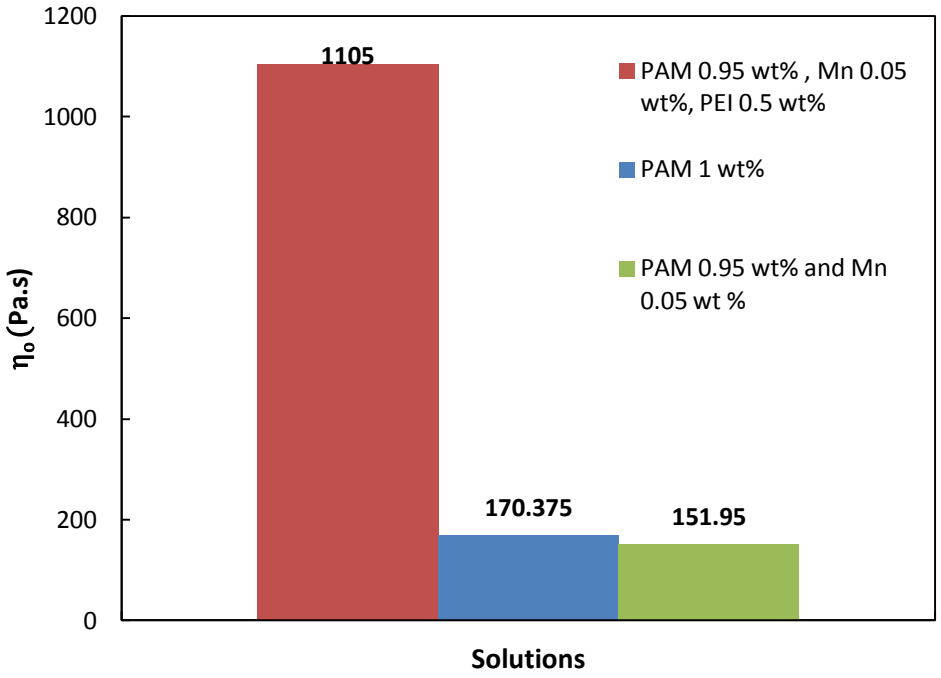

Figure 68: Comparison of viscosity of PAM with [PAM/Mn] and [PAM/Mn/PEI] solution

CONCLUSIONS & RECOMMENDATIONS

This thesis mainly dealt with studying the rheological properties of the PAM, PAM in presence of counterions and crosslinkers at various concentrations shear rate and temperature.

The metal ions used for carrying out the study were calcium, magnesium, iron and manganese. These metal ions will have a great impact on the properties of the LCM and we can take into account all these effects on the viscosity and design a suitable LCM. Also they help the solution behave in a elastic manner to take the shape of the fractures without damaging the formation. Additionally this thesis explores the gelation of PAM with crosslinker PEI in presence of manganese ions, to be used in LCM applications.

The study was dived in three different phases. The first part of the thesis dealt with studying rheology of pure PAM solution at various concentrations, shear rates and temperature.

In the second part of the thesis, we covered the effect of metal ions like magnesium, manganese, calcium and iron on the viscosity profile, thermal stability and elastic modulus of Polyacrylamide (PAM) was covered and it was deduced that addition of metal ions to PAM makes the elastic component stronger than viscous component.

Finally the thesis was concluded by crosslinking PAM with PEI to form gel in presence of manganese ions, which is best suitable for improving the elastic component of solution.

The following are the major findings of this research thesis:

- The addition of metal ions to PAM makes the elastic component stronger than viscous component i.e. to make storage modulus (G′) is stronger than loss modulus (G″), so that the gels behave more solid like elastic to take the shape of the fractures and seal them without damaging the formation.
- Reduction in thermal stability in the presence of Ca^{2+}, Mg^{2+} and Mn^{2+} was observed.
- In various [PAM/Counterion] solutions, manganese provides least reduction in viscosity when compared to similar concentration ratios of calcium, magnesium and ferric ions.
- PAM/PEI was crosslinked in presence of manganese, initially to form a very highly viscous solution with Viscosity seven to eight times more than similar concentration of pure PAM solution.
- PAM/PEI was crosslinked in presence of manganese formed a gel when heated to $65^{o}C$ and left at room temperature for 5 days. For the first time this gel formed was tested for LCM application.
- Manganese is being used for the first time in this research thesis for the preparation of LCM to make the gel formed behave elastic than viscous.
- Cross-linking is one of the possible mechanisms for LCM.

The following can be future course of work which can done in this field

- Testing the efficiency of the gel in the “Experimental set up for LCM test” at room temperature.
- Using fibrous materials to increase toughness
- Repeating the rheology at formation temperatures
- Enhancing the “Experimental set up for LCM test” to conduct experiments at formation temperature and pressure
- Testing the performance of classes of polymers and compare them with PAM.

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